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Vol. 25 August 1, 1942 No. 12

EFFECT OF EXCHANGEABLE BASES ON SOME PROPERTIES OF BALL CLAYS*

By M. D. Burdick, W. W. Meyer, and T. A. Klinefelter

Abstract

Two English and six American ball clays, representative of the ball clays in use in the whiteware industry, were tested to determine certain properties including plasticity, bulk specific gravity, volume shrinkage, transverse strength, and apparent porosity. The tests were conducted to observe the effect of electrodialysis and replacement of the cations which had been adsorbed by the clays in their natural state with other cations. Of the various cations substituted, Na^+ and K^+ were the most effective in altering certain physical properties such as plasticity and strength.

I. Introduction

The present investigation of ball clays is a continuation of studies on English china clays and American kaolins.[1] The primary purpose of these investigations was to provide data concerning the properties of the clays as types, which data might enable the manufacturers (1) to improve their products or processes of manufacture and (2) to substitute one clay for another, particularly domestic for imported clays.

Because the different properties under consideration varied considerably from one clay to another, especially from one type to another, attempts were made to determine the underlying causes of the variations. Of particular interest to manufacturers are the properties of plasticity and shrinkage as well as the strength after drying and after varying degrees of heat-treatment. In the earlier work cited,[1] the exchange capacity of each clay was found to correlate in a general way with its plasticity, shrinkage, dry strength, and fineness of grain. A commercial application of base exchange in clays is found in the treatment of fuller's earth. By processes which are virtually the same as dialyzing, the adsorbed cations in the original earth are replaced with H^+, yielding an "activated" product which often has an absorptive capacity four times that in the natural state.

In this study of ball clays, work on base-exchange capacity was emphasized because of its apparent correlation with those physical properties which account primarily for the use of these clays in whiteware bodies. Exchange capacities were determined in the preceding studies and were correlated with properties determined on the clay in what may be termed its "original" state, that is, as it was prepared for the manufacturers' use. As another step in the present study, large samples of each of the clays were electrodialyzed, portions were saturated at pH 7 with various cations, and the properties of these saturated samples as well as of samples of untreated clay, washed clay, and washed and electrodialyzed clay were determined.

All of the ball clays under consideration except clay H are representative high-grade clays in common use by whiteware manufacturers. Clay H was included because of some unusual characteristics and because it was formerly in common use. Four clays, two domestic and two English, from the same deposits as the clays used in this study were investigated in 1922 by Sortwell.[2]

II. Materials, Methods, and Apparatus

Table I gives the chemical compositions of the clays which were studied.

A combination of calomel and quinhydrone electrodes was used to determine pH values.

The amount of soluble salts present in each clay was determined by leaching a weighed sample with distilled water, evaporating the leach to dryness, and weighing.

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (White Wares Division). Received February 9, 1942.

[1] (*a*) T. A. Klinefelter, W. W. Meyer, and E. J. Vachuska, "Some Properties of English China Clays," *Jour. Amer. Ceram. Soc.*, **16** [6] 269–76 (1933).

(*b*) T. A. Klinefelter and W. W. Meyer, "Properties of Some American Kaolins and Comparison with English China Clays," *ibid.*, **18** [6] 163–69 (1935).

(*c*) W. W. Meyer and T. A. Klinefelter, "Substitution of Domestic for Imported Clays in Whiteware Bodies," *Jour. Research Nat. Bur. Standards*, **19** [1] 65–79 (1937); R.P. 1011; *Ceram. Abs.*, **16** [9] 280 (1937).

[2] H. H. Sortwell, "American and English Ball Clays," *Bur. Standards Tech. Paper*, No. 227, 30 pp., (1923); *Ceram. Abs.*, **2** [5] 101 (1923).

TABLE I

CHEMICAL COMPOSITION OF BALL CLAYS*

	Clay†							
	A	B	C	D	E	F	G	H
	Chemical composition (%)							
Loss at 110°C.	3.2	3.3	2.7	4.4	2.1	4.7	1.6	1.8
Ignition loss	9.5	16.3	11.8	16.5	12.6	13.0	10.7	8.6
SiO_2	49.8	44.2	52.0	47.2	47.7	51.3	55.1	66.3
Al_2O_3	31.3	31.6	29.5	28.5	33.3	27.9	28.2	21.0
Fe_2O_3	1.4	1.1	0.9	0.9	0.9	1.0	1.0	0.5
$TiO_2(ZrO_2)$	0.8	0.8	1.5	1.3	1.4	1.6	1.3	0.9
CaO	1.1	0.9	0.3	0.4	0.5	0.4	0.2	0.3
MgO	1.0	0.3	0.3	0.3	0.2	0.0	0.2	0.1
Na_2O	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
K_2O	1.7	1.2	0.7	0.5	1.2	0.1	1.4	0.3
Total	99.9	99.8	99.7	100.0	99.8	100.0	99.7	99.8
Total ignition loss	12.7	19.6	14.5	20.9	14.7	17.7	12.3	10.4
RO	3.9	2.5	1.3	1.2	1.9	0.5	1.8	0.7
RO_2	50.6	45.0	53.5	48.5	49.1	52.9	56.4	67.2
R_2O_3	32.7	32.7	30.4	29.4	34.2	28.9	29.2	21.5

* Analyzed by F. W. Glaze.

† Clay A, Fayles; B, Grindley; C, Kentucky No. 4; D, Kentucky dark special; E, Tennessee No. 5; F, Champion and Challenger; G, Jernigan; H, Hercules.

Figure 1 shows the processing received by those portions of the clays reserved for physical tests. The clays, as received, were ground to pass a No. 35 sieve, and a portion was set aside for the preparation of test specimens designated as "original."

The remainder was leached in a Büchner funnel in batches of 1050 gm. with distilled water, dried, ground to pass a No. 35 sieve, and a portion was reserved for the preparation of "leached-clay" specimens.

The remaining part of the leached clay was electrodialyzed in cells modified from that described by Salgado and Chapman.[3] A 60-mesh copper-screen cathode was cut to fit directly over the perforated plate of a 10-in. Büchner funnel and connected to a 115-volt direct-current supply by means of a wire through the stem of the funnel to the center of the copper screen. The cathode was separated from the clay charge by a sheet of vegetable parchment between two sheets of filter paper. The anode was made of platinum wire in a flat spiral over an "X"-frame of glass tubing which rested on the clay charge. A reservoir of distilled water maintained the water level about $1/2$ in. above the anode during the electrodialysis. The clay was considered to be sufficiently dialyzed when the dialyzate was neutral to bromthymol blue indicator. The electrodialyzed or hydrogen clay was dried and ground to pass a No. 35 sieve.

The base-exchange capacities of the clays were determined by electrometric titration of leached, electrodialyzed samples with 0.125 *N* $Ba(OH)_2$ and expressed as milliequivalents per 100 gm. of dried clay.

The organic matter active in base exchange was determined by treating 10 gm. of each clay with H_2O_2 according to the method of Olson and Bray.[4] The

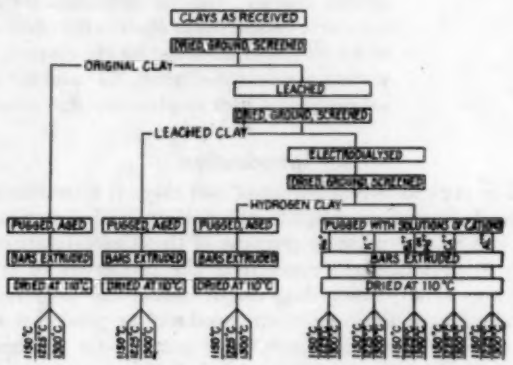

FIG. 1.—Flow sheet showing various treatments received by each clay tested.

treated clay was filtered, leached, electrodialyzed, and titrated with $Ba(OH)_2$. The difference between the base-exchange capacity of the untreated clays and H_2O_2-treated clays represents the base-exchange capacity of the organic matter at pH 7 (Table II).

The hydrogen clay was treated with the hydroxides of the various cations to the extent of the base-exchange capacity of the clay as received on the assumption that a complete exchange takes place. Clay A, for example, had a base-exchange capacity of 16.7 m.e. per 100 gm. or 167 m.e. per kg., and the sodium hydroxide was 1.088 *N*. To each kilogram of hydrogen clay, 167/1.088 ml. or 153.5 ml. of the NaOH solution were added to bring about the base exchange between H^+ and Na^+ and to produce sodium-saturated clay.

Portions of the electrodialyzed clays A and B were treated with the hydroxides of sodium, potassium, calcium, magnesium, and aluminum. In the six other clays (C to H), barium hydroxide was used instead of magnesium hydroxide. Because of the low solubility of calcium, aluminum, and magnesium hydroxides, it would have been impossible to introduce the desired amounts of these cations in solution without adding a

[3] M. L. M. Salgado and G. W. Chapman, "Simple Electrodialysis Cell for Routine Determination of Exchangeable Bases in Soils," *Soil Sci.*, **32** [3] 199–215 (1931); *Ceram. Abs.*, **10** [12] 865 (1931).

[4] L. C. Olson and R. H. Bray, "Determination of Organic Base-Exchange Capacity of Soils," *Soil Sci.*, **45**, 483 (1938).

TABLE II

MISCELLANEOUS CHEMICAL PROPERTIES OF BALL CLAYS

	Clay*							
	A	B	C	D	E	F	G	H
Water-soluble salts removed by leaching (%)	0.16	0.24	0.04	0.07	0.06	0.08	0.41	0.05
Leached clay (pH)	3.93	4.89	4.33	4.16	4.28	3.95	3.62	4.22
Clay as received (pH)	3.70	4.80	4.27	4.15	4.23	3.82	3.34	4.10
Base-exchange capacity at pH 7 of clay as received (m.e./100 gm.)	16.7	19.2	14.6	21.3	11.8	15.8	9.2	13.6
Organic matter removed by H_2O_2 treatment (%)	0.0	4.7	1.2	3.9	1.5	2.5	1.2	1.0
Clay minus organic matter (pH)	2.56	2.82	2.72	2.72	2.89	2.81	2.82	2.95
Base-exchange capacity at pH 7 of organic matter (m.e./100 gm.)	0.3	7.0	1.3	8.2	3.2	4.1	2.6	5.3

* Clay A, Fayles; B, Grindley; C, Kentucky No. 4; D, Kentucky dark special; E, Tennessee No. 5; F, Champion and Challenger; G, Jernigan; H, Hercules.

large excess of water. For this reason, these three hydroxides were mixed with the dry clays as dry reagents to which the desired amount of tempering water was added. When calcium hydroxide is added to hydrogen clay and water, the following reaction occurs:

$$\text{Hydrogen clay} + Ca(OH)_2 \longrightarrow \text{calcium clay} + 2H_2O.$$

The speed of this reaction is conditioned by the low solubility of the calcium hydroxide which results in the availability of but a limited number of calcium ions at any one time. As the reaction proceeds, the calcium ions are removed from the solution by combination as calcium clay, leaving the solution unsaturated with respect to calcium hydroxide. The reaction thus can proceed to completion, but it will obviously do so with less speed than would the similar reaction with a more soluble hydroxide.

The clay and tempering water containing the hydroxides of the various cations were mixed in a hand pug mill for 15 minutes and aged in sealed glass jars for one week. The aged clay was then placed in a deairing chamber, evacuated to a pressure of 2 cm. of mercury for 15 minutes, extruded as a column $^1/_2$ in. in diameter, and cut into bars $3^7/_8$ in. long.

The forty-eight bars of each clay, representing six specimens in each of eight conditions, were heated simultaneously in a platinum-wound resistance furnace. The temperature, which was measured by thermocouples placed in various positions in the furnace chamber, did not differ by more than 2°C. The rate of heating was controlled by a motor-driven rheostat; schedules followed are given in Tables III through X.

The volumes of the plastic bars were determined with a kerosene volumeter of the overflow type, and those of the dried and heated bars were measured with a mercury volumeter. The shrinkage during drying and heating was computed on the basis of the volume of the dry specimens. The modulus of rupture of the samples was computed by the usual formula. The dried and heated specimens were broken transversely, using a 3-in. span. The apparent porosity was determined by the 1-hr. boiling method.

III. Results of Tests

Table II gives some miscellaneous chemical properties, and Tables III to X and Figs. 2 to 5 show the physical properties of the individual clays. Each value in Tables III to X is the average for six specimens.

Some of the properties seem to have no direct correlation with others, but they are given because they may be of value in subsequent investigations.

Judged by the feel of the clays and the ease of extrusion, the original clays could not be distinguished from one another. The portions treated with KOH and those treated with NaOH, particularly, were distinctly more plastic than the original clays. The portions treated with other cations showed no marked difference in plasticity from the untreated samples.

The water of plasticity of the eight clays in the original condition varied from 25 to 47%; clays A, B, C, E, and F had values of 41% or higher, whereas clays D, G, and H had values of 39% or lower. The latter clays also showed the least shrinkage during drying. Treatment of the hydrogen clays with NaOH and with KOH resulted in lowering the water of plasticity for all clays except A and D, which were treated with KOH.

The dried strength of specimens made from NaOH-treated and KOH-treated clays was greater in all but one case, that of the KOH-treated clay A; in clay H, the increased strength was as much as 240% greater (Fig. 3). The heated specimens also showed an increase in strength but to a lesser degree.

The effect of the Na^+ and K^+ ions on the volume shrinkage during drying was somewhat erratic. Except for clay F, which was heated to 1150°C., the NaOH-treated portions of the eight clays had less shrinkage during heating than the original clays. The KOH-treated portions of most of the clays had less shrinkage during heating than the original clays; the exceptions were (1) clay A heated to 1100°C.; (2) clays A, F, and H heated to 1150°C.; (3) clays A and H heated to 1225°C.; and (4) clay H heated to 1300°C.

Substitutions of ions other than Na^+ and K^+ were less consistently beneficial. The physical properties of the Ca clays, Mg clays, and Ba clays were not greatly different from those of the clays in their original state. Compared with the original clay specimens, those of hydrogen clay and of hydrogen clay treated with $Al(OH)_3$ showed higher water of plasticity, lower bulk specific gravity both in the dried condition and*

* Continued on p. 335.

TABLE III

PHYSICAL PROPERTIES OF CLAY A*

Condition	Water of plasticity (%)	Bulk specific gravity				Volume shrinkage (%)				Transverse strength (lb./sq. in.)				Apparent porosity (%)		
		Dry	1100°C.	1150°C.	1225°C.	Dry	1100°C.	1150°C.	1225°C.	Dry	1100°C.	1150°C.	1225°C.	1100°C.	1150°C.	1225°C.
Original	42.0	1.763	2.440	2.482	2.510	35.7	34.5	35.8	36.3	840	10700	11100	11500	0.0	0.0	0.0
Leached	46.9	1.740	2.443	2.487	2.514	42.9	35.8	36.8	37.5	860	12100	10800	12200	.0	.0	.0
Saturated																
H^+	50.6	1.668	2.407	2.472	2.518	45.9	37.1	39.1	40.0	780	13300	14000	13600	.1	.0	.0
Al^{+++}	49.7	1.658	2.389	2.464	2.512	47.7	37.2	39.2	40.3	730	12200	13000	13200	.0	.0	.0
Ca^{++}	44.2	1.793	2.464	2.491	2.517	46.6	33.9	34.7	35.2	920	12700	11800	12400	.0	.0	.0
Mg^{++}	43.6	1.809	2.458	2.479	2.498	46.8	33.4	34.2	34.5	1030	12400	12500	13700	.0	.0	.0
K^+	46.9	1.659	2.426	2.476	2.500	40.0	37.8	39.1	39.8	740	12200	11100	15300	.0	.0	.0
Na^+	36.2	1.919	2.443	2.453	2.463	40.5	28.5	29.0	29.2	1680	11700	14200	13900	.0	.0	.0

* Heating rate, 50°/hr. to test temp.; soaked 1 hr.

TABLE IV

PHYSICAL PROPERTIES OF CLAY B*

Condition	Water of plasticity (%)	Bulk specific gravity				Volume shrinkage (%)				Transverse strength (lb./sq. in.)				Apparent porosity (%)		
		Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.
Original	43.8	1.545	2.002	1.889	2.108	31.8	36.8	33.6	40.9	980	6400	4800	6300	0.7	4.6	0.3
Leached	46.1	1.562	2.075	1.938	2.188	35.8	37.6	33.3	41.2	1030	7200	5900	8600	.5	3.3	.1
Saturated																
H^+	47.8	1.479	2.191	2.201	2.271	30.9	43.7	43.9	46.0	670	8200	7900	8200	.1	0.7	.1
Al^{+++}	48.2	1.476	2.184	2.204	2.266	31.2	43.8	44.3	46.1	670	8600	8900	9000	.1	0.6	.1
Ca^{++}	46.2	1.564	2.155	2.058	2.224	33.5	39.8	37.1	41.9	1050	7500	6700	8100	.1	1.5	.1
Mg^{++}	44.7	1.576	2.145	1.994	2.234	33.7	38.8	34.2	41.5	1050	7800	6000	8400	.1	3.6	.1
K^+	40.9	1.654	2.159	2.075	2.237	35.4	35.5	33.0	38.4	1700	7900	6900	9300	.1	1.6	.1
Na^+	37.5	1.742	2.109	1.975	2.118	35.2	30.2	25.3	31.5	2130	8000	7100	7900	.1	1.8	.4

* Columns (1): All bars black-cored except those of H^+-saturated and Al^{+++}-saturated clay; heating rate, 50°/hr. to test temp.; soaked 1 hr.; columns (2): completely oxidized; heating schedule, 30°/hr. to 700°C.; 20°/hr. to 860°C.; 30°/hr. to 1160°C.; 45°/hr. to 1300°C.; soaked 1 hr.

TABLE V

PHYSICAL PROPERTIES OF CLAY C*

Condition	Water of plasticity (%)	Bulk specific gravity				Volume shrinkage (%)				Transverse strength (lb./sq. in.)				Apparent porosity (%)		
		Dry	1150°C.	1225°C.	1300°C.	Dry	1150°C.	1225°C.	1300°C.	Dry	1150°C.	1225°C.	1300°C.	1150°C.	1225°C.	1300°C.
Original	46.6	1.635	2.134	2.258	2.353	40.2	32.7	36.3	38.8	410	6300	10000	10500	15.9	0.8	0.1
Leached	43.5	1.652	2.146	2.256	2.334	37.2	32.4	35.8	38.2	410	7800	8000	9600	14.9	0.5	.4
Saturated																
H^+	47.7	1.536	2.038	2.214	2.341	31.7	33.8	39.0	42.1	280	5900	9300	10900	20.8	8.6	.1
Al^{+++}	45.2	1.569	2.066	2.228	2.356	24.7	33.2	38.2	41.7	290	6800	8200	10100	19.9	8.9	.2
Ca^{++}	41.0	1.674	2.172	2.263	2.357	33.0	32.2	35.0	37.6	410	7300	8300	10000	14.4	1.1	.8
Ba^{++}	40.9	1.680	2.199	2.309	2.381	31.8	32.6	36.1	38.0	470	8100	10100	10000	13.8	0.1	.1
K^+	36.4	1.735	2.248	2.385	2.411	26.5	32.0	36.1	36.5	520	8000	9700	13500	8.5	0.4	.1
Na^+	36.5	1.797	2.242	2.314	2.362	33.2	29.2	31.4	32.9	800	11600	12100	11500	1.0	0.2	.1

* Heating rate, 50°/hr. to test temp.; soaked 1 hr.

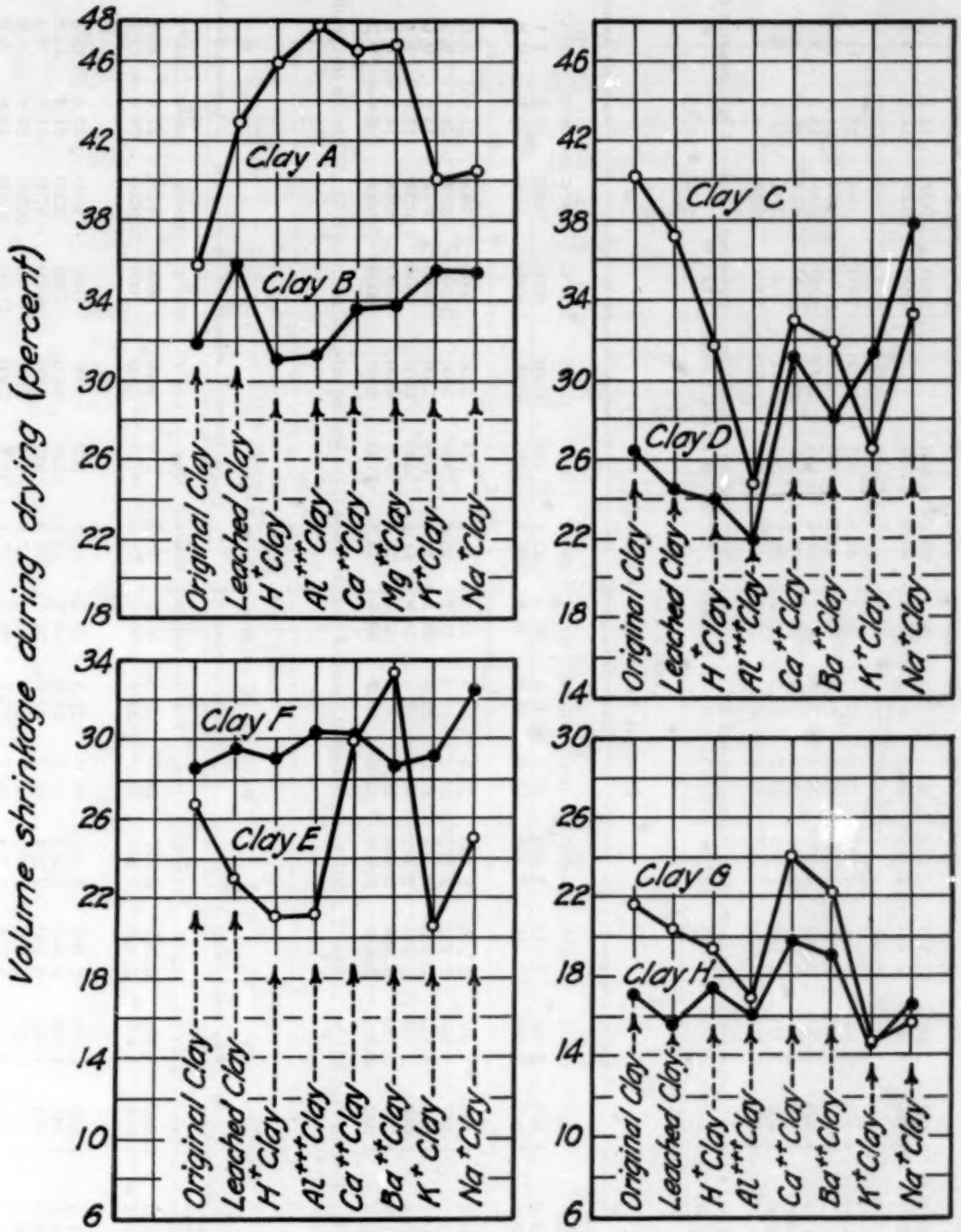

FIG. 2.—Volume shrinkage during drying of test pieces of eight clays in condition as received and after several treatments indicated.

TABLE VI

PHYSICAL PROPERTIES OF CLAY D*

Condition	Water of plasticity (%)	Bulk specific gravity				Volume shrinkage (%)				Transverse strength (lb./sq. in.)				Apparent porosity (%)		
		Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.
Original	39.3	1.611	2.061	2.111	2.211	26.4	35.3	36.8	39.7	600		9500	9000	12.3	1.5	0.1
Leached	39.4	1.602	2.046	2.101	2.211	24.5	35.2	36.9	40.0	530		9800	10400	13.8	1.6	.1
Saturated																
H^+	45.4	1.475	1.881	2.020	2.210	24.0	35.1	39.8	44.9	400	13100	7800	11100	24.3	17.0	.1
Al^{+++}	45.2	1.467	1.872	2.027	2.203	21.9	34.9	39.9	44.7	340	9400	8700	10300	24.6	16.8	.1
Ca^{++}	46.1	1.536	2.006	2.041	2.166	31.1	36.6	37.8	41.4	450	18200	9900	10300	15.5	8.7	.2
Ba^{++}	45.6	1.539	2.004	2.094	2.219	28.0	36.0	38.7	42.2	540	13400	8000	10800	18.0	3.5	.1
K^+	39.6	1.657	2.117	2.182	2.225	31.3	34.7	36.7	38.7	720	13800	7100	7100	6.7	0.8	.4
Na^+	38.4	1.758	2.047	2.050	2.205	37.8	28.0	28.2	33.7	790	15400	5900	10300	9.9	4.2	.2

* Columns (1): All bars black-cored except those of H^+-saturated and Al^{+++}-saturated clay; heating rate, 50°/hr. to test temp.; soaked 1 hr.; columns (2): completely oxidized; heating schedule, 25°/hr. to 600°C.; 13°/hr. to 840°C.; 30°/hr. to 1000°C.; 50°/hr. to 1300°C., soaked 1 hr.

TABLE VII

PHYSICAL PROPERTIES OF CLAY E*

Condition	Water of plasticity (%)	Bulk specific gravity				Volume shrinkage (%)				Transverse strength (lb./sq. in.)				Apparent porosity (%)		
		Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.
Original	42.0	1.609	2.061	2.318	2.409	26.7	32.1	39.6	42.1	460	6600	9600	10600	18.9	1.1	0.1
Leached	38.4	1.642	2.095	2.336	2.424	23.0	31.9	38.8	41.2	480	6800	8500	8700	18.0	0.8	.2
Saturated																
H^+	40.5	1.538	1.956	2.289	2.456	21.1	31.4	41.5	45.5	350	5100	9000	9800	21.4	8.6	.1
Al^{+++}	42.1	1.537	1.954	2.282	2.461	21.2	31.5	41.4	45.6	360	5500	10200	8200	24.4	9.2	.1
Ca^{++}	40.1	1.668	2.151	2.355	2.418	29.9	32.5	38.3	39.8	620	7500	9700	10400	15.6	0.5	.1
Ba^{++}	42.8	1.647	2.130	2.346	2.441	33.3	32.6	38.9	41.1	540	6000	8800	10200	17.3	1.1	.0
K^+	31.9	1.716	2.185	2.389	2.458	20.6	31.5	37.3	39.0	970	6500	8600	8800	14.8	0.1	.1
Na^+	29.6	1.832	2.256	2.379	2.406	25.0	29.2	32.7	33.5	1130	6800	10500	9500	8.4	0.2	.8

* Columns (1): Heating rate, 25°/hr. to 1000°C.; 50°/hr. to test temp.; soaked 1 hr.; columns (2): heating rate, 25°/hr. to 600°C.; 40°/hr. to test temp.; soaked 1 hr.

TABLE VIII

PHYSICAL PROPERTIES OF CLAY F*

Condition	Water of plasticity (%)	Bulk specific gravity				Volume shrinkage (%)				Transverse strength (lb./sq. in.)				Apparent porosity (%)		
		Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.
Original	41.0	1.630	1.854	2.207	2.277	28.5	23.8	36.2	38.3	770	4600	8900	10100	27.6	10.6	0.7
Leached	41.1	1.618	1.849	2.196	2.266	29.4	23.4	36.5	38.5	710	5500	7600	8700	28.9	11.3	0.9
Saturated																
H^+	44.5	1.549	1.700	2.162	2.226	28.9	21.3	38.2	40.1	560	5000	7800	8600	33.5	15.3	8.8
Al^{+++}	46.5	1.540	1.686	2.146	2.215	30.3	21.2	38.2	40.1	520	4300	7300	8200	34.4	15.8	9.5
Ca^{++}	40.0	1.681	1.989	2.190	2.274	30.2	27.0	33.7	36.4	940	6400	8600	9700	21.6	9.4	0.2
Ba^{++}	39.6	1.670	1.953	2.236	2.302	28.6	26.1	35.5	37.5	910	6100	8000	10500	23.9	8.6	0.2
K^+	37.1	1.701	2.025	2.298	2.338	29.1	27.3	36.0	37.1	1180	5500	11400	10400	19.9	0.5	0.4
Na^+	33.7	1.834	2.147	2.262	2.298	32.4	26.2	29.9	31.1	2060	7100	9800	11600	9.4	0.1	0.3

* Columns (1): Heating rate, 25°/hr. to 1000°C.; 50°/hr. to test temp.; soaked 1 hr.; columns (2): heating rate, 25°/hr. to 600°C.; 50°/hr. to test temp.; soaked 1 hr.

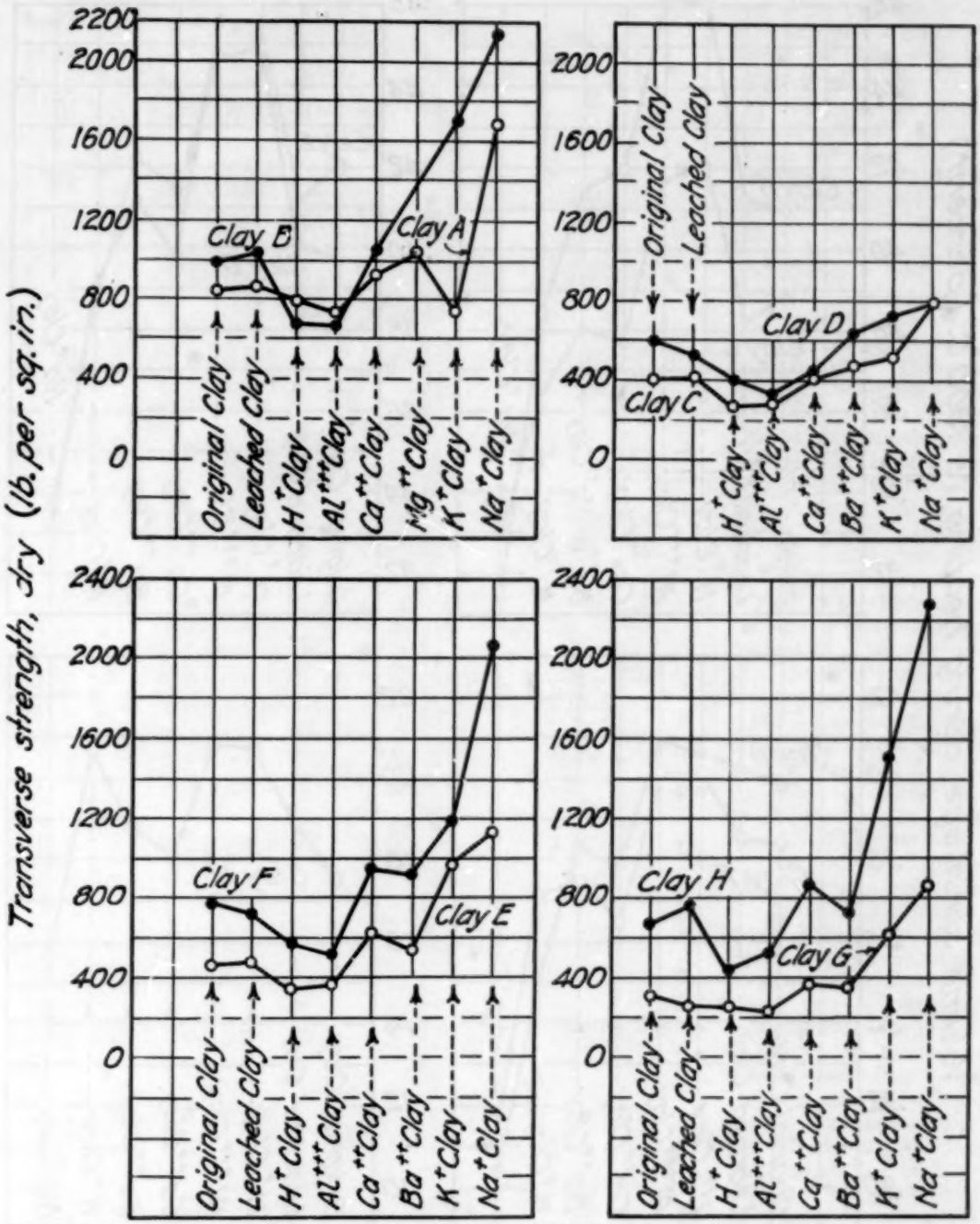

FIG. 3.—Transverse strength of dry bars of eight clays in condition as received and after several treatments indicated.

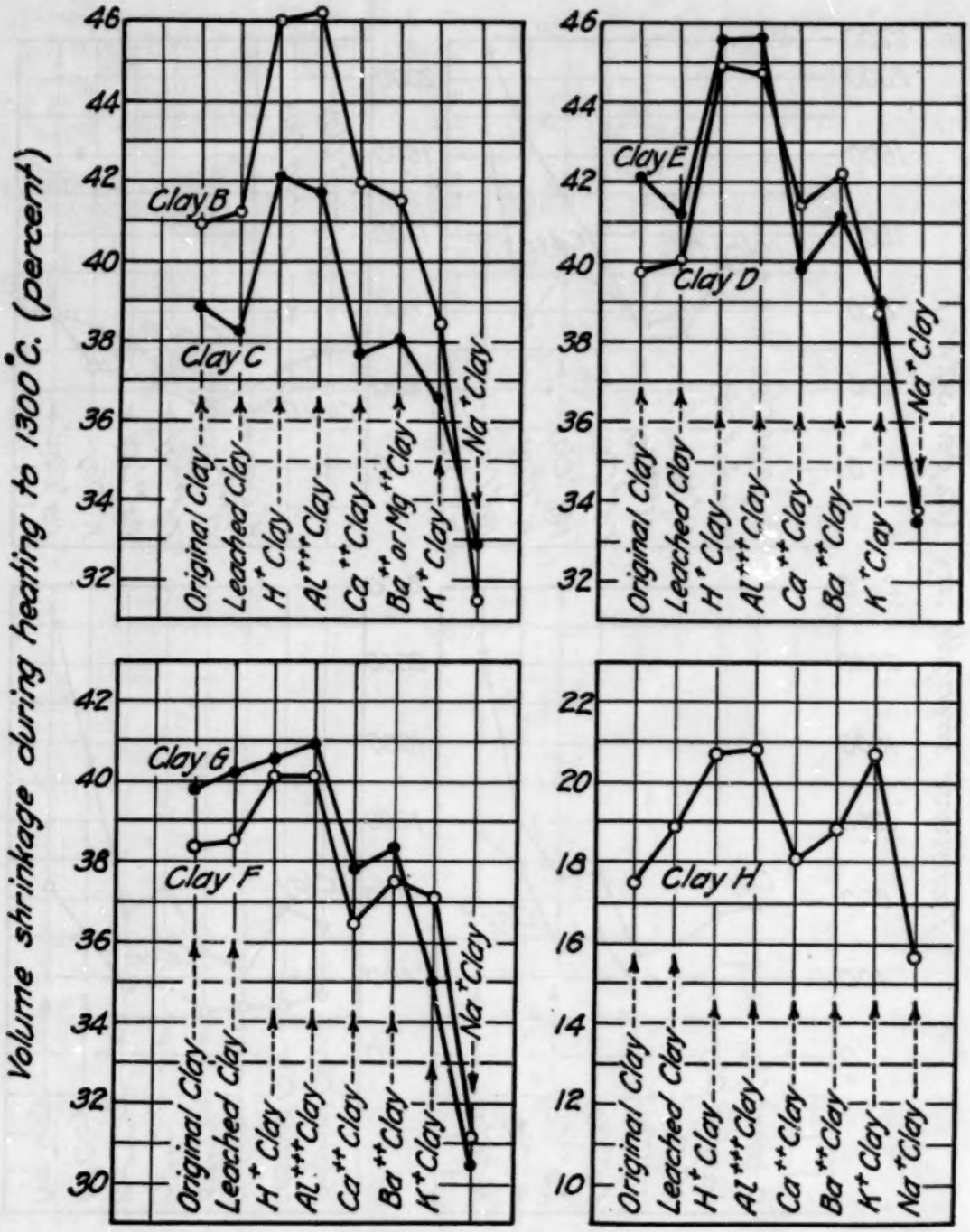

FIG. 4.—Volume shrinkage during heating to 1300 °C. of test pieces of seven clays in condition as received and after several treatments indicated.

TABLE IX

PHYSICAL PROPERTIES OF CLAY G*

Condition	Water of plasticity (%)	Bulk specific gravity			Volume shrinkage (%)			Transverse strength (lb./sq. in.)			Apparent porosity (%)		
		Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	Dry	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.	(1) 1150°C.	(1) 1225°C.	(2) 1300°C.
Original	37.7	1.597	1.877	2.145	2.371	21.6	24.2	33.7	39.8	310	3200	6200	10800	27.5	14.9	0.1
Leached	38.4	1.586	1.873	2.122	2.376	20.4	24.2	33.1	40.2	260	4400	6400	10500	26.5	16.9	.4
Saturated																
H^+	38.3	1.574	1.851	2.100	2.363	19.4	23.8	32.9	40.5	250	6000	7000	11000	29.9	17.9	.2
Al^{+++}	38.4	1.554	1.830	2.069	2.347	16.9	23.9	33.1	40.9	230	4500	5800	9500	30.7	19.0	.6
Ca^{++}	37.6	1.648	1.937	2.181	2.380	24.0	24.1	32.4	37.8	370	5400	6800	9200	24.8	13.3	.0
Ba^{++}	38.7	1.629	1.935	2.138	2.365	22.1	24.5	32.0	38.3	350	5600	7500	7300	26.6	15.2	.1
K^+	29.3	1.736	2.035	2.231	2.388	14.8	23.6	30.2	35.0	620	5600	10400	6700	22.3	11.3	.1
Na^+	26.3	1.838	2.103	2.265	2.363	15.7	21.8	27.4	30.4	860	5 00	7300	8100	18.1	8.7	.3

* Columns (1): Heating rate 25°/hr. to 1000°C.; 50°/hr. to test temp.; soaked 1 hr.; columns (2): heating rate, 25°/hr. to 600°C.; 35°/hr. to test temp.; soaked 1 hr.

TABLE X

PHYSICAL PROPERTIES OF CLAY H*

Condition	Water of plasticity (%)	Bulk specific gravity			Volume shrinkage (%)			Transverse strength (lb./sq. in.)			Apparent porosity (%)		
		Dry	1150°C.	1225°C.	1300°C.	Dry	1150°C.	1225°C.	1300°C.	Dry	1150°C.	1225°C.	1300°C.	1150°C.	1225°C.	1300°C.
Original	24.7	1.872	1.940	2.058	2.073	17.1	11.9	16.9	17.5	670	3100	4100	4200	26.5	21.9	19.3
Leached	25.2	1.881	1.973	2.095	2.112	15.7	13.1	18.4	18.9	700	3600	4700	4600	25.1	19.5	17.0
Saturated																
H^+	28.6	1.775	1.831	2.009	2.041	17.4	11.7	19.6	20.7	440	2600	3500	4200	31.3	24.4	21.3
Al^{+++}	28.3	1.778	1.833	2.010	2.044	16.2	11.6	19.5	20.8	520	2700	3500	4400	31.1	24.1	21.2
Ca^{++}	26.6	1.886	1.990	2.085	2.101	19.8	13.9	17.4	18.1	860	3600	4800	4700	24.4	19.7	17.9
Ba^{++}	27.0	1.865	1.974	2.079	2.096	19.1	13.7	18.1	18.8	720	3600	4600	4700	25.6	21.1	18.3
K^+	20.6	1.964	2.077	2.192	2.261	14.4	13.7	18.1	20.7	1510	4200	4700	5200	20.7	14.2	8.3
Na^+	19.7	2.039	2.126	2.193	2.208	16.5	12.6	15.2	15.6	2270	4300	5800	5400	17.0	12.3	9.8

* Heating rate, 25°/hr. to 1000°C.; 50°/hr. to test temp.; soaked 1 hr.

after heating, lower shrinkage during drying, higher shrinkage during heating, higher apparent porosity when heated below temperatures at which vitrification becomes nearly complete, and lower transverse strength.

Two of the ball clays (B, English, and D, Kentucky) black-cored when heated on the schedule which had been satisfactory for clays A and C. The worst black-coring in clays B and D was shown by the NaOH-treated and KOH-treated samples; samples of the untreated clay also exhibited this phenomenon to some extent, but the H^+-saturated and $Al(OH)_3$-treated specimens were free from it. Figure 5 shows that the hydrogen clay and the $Al(OH)_3$-treated clay specimens remained consistently more porous than the others when they were heated below the temperature at which vitrification became complete, but at 1300°C., they had practically the same porosity as the other specimens. Because clay B was practically vitrified at the lowest heating temperature (1150°C.), no determination of apparent porosity was made after it was heated to temperatures well below that at which vitrification became complete. The fact that neither the hydrogen clay nor the $Al(OH)_3$-treated specimens of this clay black-cored is indirect evidence that an open structure similar to that shown for clay D (Fig. 5) was maintained prior to vitrification.

Similarity of the properties of the $Al(OH)_3$-treated specimens to those of the hydrogen clay indicates that there was little if any replacement of the H^+ ions by Al^{+++} ions, even though the most finely divided $Al(OH)_3$ was prepared for use in this work.[5] This

[5] R. H. Ewell and Herbert Insley, "Hydrothermal Synthesis of Kaolinite, Dickite, Beidellite, and Nontronite," *Jour. Research Nat. Bur. Standards*, 15 [2] 173–86 (1935); R.P. 819; p. 177; *Ceram. Abs.*, 14 [11] 290 (1935).

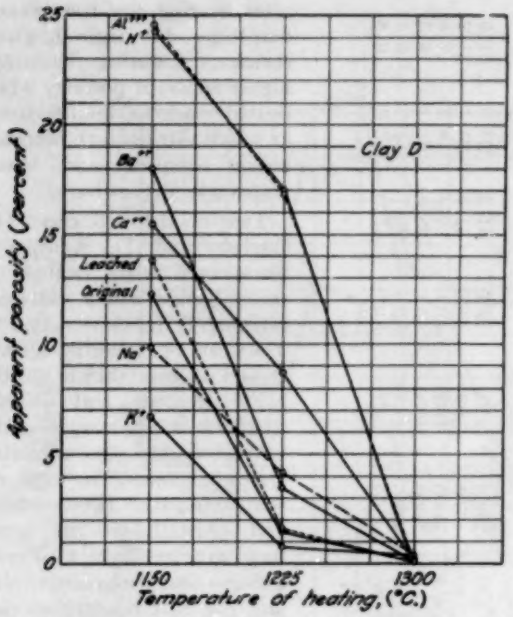

FIG. 5.—Apparent porosity of test pieces of clay D heated to three different temperatures.

evidence is further substantiated by the fact that when clay pastes containing the requisite amount of $Al(OH)_3$ were tested with bromthymol blue, they were indicated to be fairly strongly acidic.

IV. Summary

Some of the physical properties of eight ball clays tested in the condition as received and after various base-exchange treatments were determined. Several of the treatments produced minor changes in the properties of plasticity, bulk specific gravity, volume shrinkage, transverse strength, and apparent porosity. Saturation at pH 7 of leached, electrodialyzed clay with Na^+ and K^+ ions resulted in significant and, in general, beneficial changes in most of these properties. Na^+- and K^+-treated clays required less tempering water and were more plastic. They also had greater transverse strength in the dried condition and to a lesser degree after heating, and they had less shrinkage during heating than the original or untreated clays. Results on two clays containing excessive amounts of organic matter indicated that the organic matter in the clays was more readily oxidized during heat-treatment when the clay was saturated with H^+ ions or when H^+ saturated clay was treated with $Al(OH)_3$ than in any other condition tested.

Acknowledgment

The authors acknowledge their indebtedness to F. W. Glaze, who made the chemical analyses given in Table I.

NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

FUNDAMENTAL STUDY OF CLAY: III, CASTING AS A BASE-EXCHANGE PHENOMENON*

BY A. L. JOHNSON† AND F. H. NORTON

ABSTRACT

Specimens of commercial casting slip were cast in plaster molds, porous bisque molds, and porous bisque molds treated with calcium and aluminum chloride. A qualitative determination of the ion serving in the exchange position is possible by the evaluation of the yield value of the cast specimen. The results on a series of tests indicate that casting clayware may be carried out by one of two processes, namely, mechanical water removal by the porous mold or by an exchange reaction between the ions of the slip and those of the mold; combinations of both processes may also occur. A detailed description of both methods, including practical applications, is given.

I. Introduction

Porous plaster molds have been used for the fabrication of ceramic ware as far back as the 18th century.[1] Their chief function was simply that of water absorption, leaving the formed clay pieces in a semidried condition. This process of forming ware by allowing a clay–water system to be in contact with an absorbent plaster mold for the partial removal of the water is known as the casting process.

Investigators have shown that the actual mechanism

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† Prepared from material in a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology, Cambridge, Mass.

[1] A. Brongniart, Traité des Arts Céramique, Vol. II. Bechet Jeune, Paris, 1854.

of casting is chiefly the removal of some of the water from the clay–water system in contact with the plaster mold which leaves the system in a rigid state. In support of this viewpoint, Matzen and Parmelee[2] have shown that the initial water content of the plaster mold controls the casting rate. Hind[3] believes that when the slip is poured from the mold after the casting process, it has a lower proportion of water than that originally used. It is also common commercial practice to dry plaster molds after their use to condition them for subsequent casting operations.

Although the majority of evidence seems to indicate that the casting mechanism is a mechanical dewatering of the clay slip, certain factors point toward a mechanism which, if not actually responsible for the casting operation as it is carried out, should be considered as a definite possibility. Weber[4] believes that the plaster mold serves a double function in the casting operation and that "liquefaction" of clays by alkalis is a reaction whose success depends on the absence of the sulfate radicle. He reasons, therefore, that in addition to partial dewatering of the slip, the plaster mold introduces the sulfate radicle and that this ion causes a sol-gel transformation of the slip. Hall[5] is inclined to agree with Weber, but he includes other factors which may influence the sol-gel transformation. Wiss, Camp, and Ladoo[6] show that the calcium sulfate ($CaSO_4$) mold reacts with the sodium silicate (Na_2SiO_3) and carbonate (Na_2CO_3), which are frequently used as deflocculents.

These ideas admittedly offer no conclusive evidence in support of a theory of casting other than that of water absorption. The colloidal nature of clay, however, is such that ideas of this type could be put into use as means for casting clayware. Bleininger,[7] in support of this theory, applied for a patent on the use of aluminum sulfate to be added to deflocculated slips, which resulted in a delayed coagulating action after the slip was poured in the mold. If this coagulating action could be brought about by the reaction of the slip and the mold into which the slip had been placed, it would eliminate the need for the introduction of the flocculent prior to pouring and thus utilize the excellent pouring properties of the deflocculated slip.

Lambie and Ross[8] have recommended an ingenious method for casting clay blocks which utilizes yet another colloidal property of the clay–water system. A highly thixotropic system is poured into a mold, which in this case need not be highly absorbent. The slip and mold are constantly vibrated during the pouring operation until the mold is filled; the thixotropic behavior of the system is such that when vibration ceases the system sets and sufficient yield value is present to permit the removal of the mold for the drying operation.

Clays possess a property which enables them to exchange certain ions, and by such a reaction the characteristics of the system are altered. If it were possible to transform the clay, while it is in contact with the mold during the casting operation, to some form which would give it rigidity, the operation by this exchange reaction would constitute casting.

The object of this study was to investigate the possibility of utilizing such an exchange reaction between the deflocculated clay slip and the mold in order to cast ceramic ware successfully.

II. Theoretical Considerations

Modern concepts of the colloidal nature of clays and the properties of these clays in the varied colloidal states in which they exist indicate many avenues worthy of consideration. The elimination of several of these suggestions is possible by a logical analysis of the properties of clay which are best suited to a ceramic cast.

A freshly cast clay piece, for example, may have a water content in the range of 15 to 18% (wet basis). The rigidity of the system is important, inasmuch as the distortion of the wet piece is possible whether the ware is stationary or in motion. To be more specific, the yield value of the system has marked significance when the cast is first removed from the mold as well as when it is handled in later processes. After the mold is opened and the cast is removed, the process of joining two or more sections on to the main body, known as "sticking," requires that the parts to be connected have identical workability. A clay cast whose workability is sensitive to slight changes in water content requires special care. The trimming operation also depends on this property so that, in an ideal case, a clay cast which has high plasticity at this stage and is insensitive to slight changes in water content would be most effective.

The shrinkage characteristics of the system are also important. If the shrinkage in core casting proceeds at a rapid rate, cores must be pulled at the time when the cast has released itself from the mold but has not yet begun to shrink about the core. This point is extremely critical in industrial processes. The mold, furthermore, must be opened and the cast removed before shrinkage, which is proceeding at a rapid rate, causes undue stresses or, finally, cracking. In the ideal case under consideration, therefore, a cast containing a clay form which has low shrinkage and high extensibility could be used to advantage. These qualities of a clay system, which are desirable in the best cast according to industrial concepts, may be

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[2] H. B. Matzen and C. E. Parmelee, "Air Conditioning in Ceramics," *Jour. Amer. Ceram. Soc.*, **13** [11] 856–64 (1930).

[3] S. R. Hind, "Study of Factors Involved in Slip Casting," *Trans. Ceram. Soc.* [England], **22**, 90–104 (1923); *Ceram. Abs.*, **3** [1] 17 (1924).

[4] E. Weber, "Liquefaction of Clays by Alkalis and Use of Fluid Clay Casting in Ceramic Industry" (translation), *Trans. Ceram. Soc.* [England], **8**, 11–22 (1909).

[5] F. P. Hall, "Casting of Clayware, a Résumé," *Jour. Amer. Ceram. Soc.*, **13** [10] 751–66 (1930).

[6] J. E. Wiss, T. P. Camp, and R. B. Ladoo, "Gypsum Plaster in the Ceramic Industry," *ibid.*, **13** [5] 287–314 (1930).

[7] A. V. Bleininger, "Process of Forming Ceramic Products," U. S. Pat. 1,528,908, March 10, 1925; *Ceram. Abs.*, **4** [5] 152 (1927).

[8] J. M. Lambie and D. W. Ross, "Mold for Casting Clay Blocks and Method of Molding," U. S. Pat. 1,625,947, April 26, 1927; *Ceram. Abs.*, **6** [7] 297 (1927).

summarized as (*a*) high yield point, (*b*) high workability and plasticity, and (*c*) low shrinkage and high extensibility.

Because casting is commonly assumed to be merely a dewatering operation, the properties of the clay as it exists in the deflocculated slip should be analyzed; this form of clay should also be present in the cast piece if dewatering has been the only change. Sodium clays are generally believed to produce the best casting slips because of their high fluidity, and, according to the most recent concepts on the preparation of deflocculated slips,[9] reactions 1(*a*) and 1(*b*) take place. Commercial clays usually exist in the calcium or magnesium[10] form, probably owing to the presence of some soluble salt of these elements, and when the common deflocculents are introduced an exchange of cations occurs as follows:

$$(\text{Clay OH})_2\text{Ca} + \text{CaSO}_4 + \text{Na}_2\text{SiO}_3 \longrightarrow 2[\text{clay OH–Na}] + \textit{CaSiO}_3 + \text{Na}_2\text{SO}_4. \quad (1a)$$

$$(\text{Clay OH})_2\text{Ca} + \text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow 2[\text{clay OH–Na}] + \textit{CaCO}_3 + \text{Na}_2\text{SO}_4. \quad (1b)$$

The addition of an excess of the deflocculents (Na_2SiO_3 and/or Na_2CO_3) makes the system alkaline, and the conditions for deflocculation are satisfied,[9] namely, the production of clay OH–Na in an alkaline medium. Johnson and Norton[9] show that the presence of the sulfate ion ($SO_4^{=}$) may interfere with the deflocculation process but that it may be removed by treatment with barium carbonate. Lambe[11] shows that the viscosity of the slip can be reduced by barium carbonate ($BaCO_3$) treatment. This lowered viscosity, in effect, is due to a more complete deflocculation brought about by the precipitation of the sulfate ion ($SO_4^{=}$) according to the reaction,[9]

$$\text{Na}_2\text{SO}_4 + \text{BaCO}_3 \longrightarrow \textit{BaSO}_4 + \text{Na}_2\text{CO}_3. \quad (2)$$

The deflocculated casting slip in any event contains the clay OH–Na form, and the properties of this clay should be compared with those which have been enumerated for an ideal cast.

Speil[12] has compared the plasticity, yield points, and shrinkage of monodisperse fractions of kaolinite in various forms. Hauser and Johnson[13] believe that the plasticity and yield points of clay systems would decrease in the order of clay OH–H, (clay OH)$_3$R, (clay OH)$_2$R, and clay OH–R, wherein *R* denotes any cation of the proper valency. Drawing from a large amount of unpublished data,* the properties of each form of clay shown in Table I appear to be in their proper respective positions relative to one another.

TABLE I

RELATIVE PROPERTIES OF CLAY FORMS*

	Clay OH–H	(Clay OH)$_3$Al	(Clay OH)$_2$Ca	Clay OH–Na
Plasticity†	4	3	2	1
Yield point†	4	3	2	1
Shrinkage‡	1	2	3	4

* These data constitute work which has been done in connection with the program on the Fundamental Clay Research.
† See references 12 and 13.
‡ See reference 12.

Table I shows that, for the optimum properties of the cast as previously discussed, clay OH–Na is the least desirable form. The reasons for the use of this clay form in casting slips, however, are based on the conception of casting which predominates at this time. Casting, which is a dewatering operation, requires the use of a high specific gravity slip because the casting time is shorter owing to the necessity of the removal of smaller quantities of water before the slip becomes rigid and a cast is obtained. This effect is shown in Fig. 1 (curve *A*), where the apparent viscosity of the slip used throughout this work is plotted against water content (wet basis) at constant electrolyte content. The properties of this system indicate that viscosity changes are small up to a definite specific gravity value (1.68 or 34% of H_2O) of the slip. For specific gravity values above this point, however, the viscosity values are altered greatly by very small decreases in the amount of water in the slip. Thus any value of specific gravity below 1.81 or 1.80 is satisfactory for pouring this slip into a mold, and as soon as the porous mold has removed sufficient water to cause the system to become rigid, a cast may be obtained. According to Fig. 1, whether the slip is introduced to the mold at 26.75% of water (1.80 specific gravity) or at 34% of water (1.68 specific gravity) has no effect on the point where the cast would display sufficient rigidity to be removed from the mold. From the standpoint of casting time required, however, the water content of the original slip is important; for example, the higher the specific gravity of the slip the shorter the casting time, and the higher the specific gravity of the slip the lower the shrinkage in drying.

The ideal condition, however, would be to utilize the excellent pouring properties of the relatively dense clay OH–Na slip; then, by an exchange reaction, the clay of the slip may be converted to any other of the three remaining forms shown in Table I and the benefits of this form of clay in the final cast may be obtained.

[9] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: II, Mechanism of Deflocculation in Clay–Water System," *Jour. Amer. Ceram. Soc.*, **24** [6] 189–203 (1941).
[10] R. P. Graham and J. D. Sullivan, "Critical Study of Methods of Determining Exchangeable Bases in Clays," *ibid.*, **21** [5] 176–83 (1938).
[11] C. M. Lambe, Jr., "Control of Clays Containing Varying Quantities of Adsorbed Salts," *Bull. Amer. Ceram. Soc.*, **20** [5] 155–58 (1941).
[12] S. Speil, "Effect of Adsorbed Electrolytes on Properties of Monodisperse Clay–Water Systems," *Jour. Amer. Ceram. Soc.*, **23** [2] 33–38 (1940).
[13] E. A. Hauser and A. L. Johnson, "Plasticity of Clays," *ibid.*, **25** [May 1, No. 9] 223–37 (1942).

* See star footnote, Table I.

A study of the kinetics involved in such a colloidal reaction, according to the concepts set forth by Hauser and Hirshon[14] and later applied specifically to the clay–water system by Johnson and Norton,[9] reveals that kaolinite in the clay OH–Na form is at a relatively high energy level. This form of clay, therefore, under the following conditions, has a tendency to revert to any lower form, namely, (clay OH)$_2$R, (clay OH)$_3$R, or clay OH–H. According to this line of reasoning, the fact that plaster molds ($CaSO_4$) are used for casting brings up the question as to why the following exchange reaction does not occur between the clay OH–Na of the slip and the calcium sulfate of the mold:

$$2[\text{Clay OH–Na}] + CaSO_4 \longrightarrow (\text{clay OH})_2Ca + Na_2SO_4. \quad (3)$$

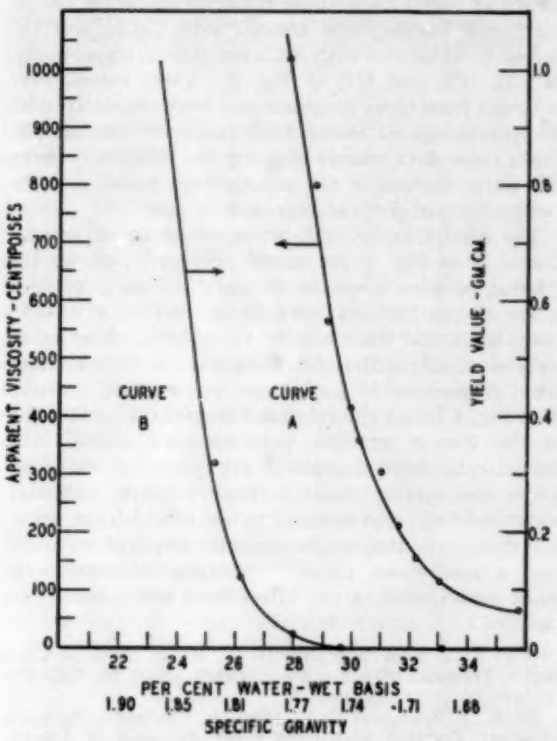

FIG. 1.—Relation between apparent viscosity (curve *A*), yield point (curve *B*), and percentage of water in slip.

The answer may be (*a*) that reaction (3) may occur but has not been reported or (*b*) that a more probable reaction, as far as the energy considerations of the system are concerned, may be occurring which thereby prevents the reaction shown in equation (3). The reaction* that may have preference is taking place between the mold and the deflocculent† as follows:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaSiO_3 + Na_2SO_4. \quad (4a)$$

$$CaSO_4 + Na_2SiO_3 \longrightarrow CaCO_3 + Na_2SO_4. \quad (4b)$$

Equations 4(*a*) and 4(*b*) show that if this reaction is preferred, the presence of sodium sulfate, which is formed by the double decomposition, would prevent further dissociation of $CaSO_4$ into Ca^{++} and $SO_4^{=}$ ions by common ion effect owing to the low solubility of the calcium sulfate. This repression of the ionization of the $CaSO_4$ of the mold would prevent the exchange reaction of equation (3). If the kinetics of the system were such that the reaction according to equation (3) takes precedence over that given by equations (4), it is possible that this phase of the casting process has not been fully investigated and that a more comprehensive study on the casting mechanism is needed.

At this point of theoretical reasoning, it is worth while to consider how the identification of the various forms of clay may be made. A chemical analysis obviously would not reveal what cations are serving in the exchange positions because the system is very complex. A qualitative comparison, however, between two or more samples of clay may be possible by determining the yield value of the system. Such results could indicate the type of cation serving in the exchange position of a particular sample by the relative yield value obtained. This suggestion is based on theoretical[15] and experimental data†, which indicate that the yield value of clay systems decreases from clay OH–H through clay OH–Na. In view of this discussion, the specific problem of this paper may now be restated. It would be advantageous, first, to determine if casting in plaster molds is entirely a dewatering process, which could be accomplished by a qualitative comparison of the form of clay as it exists in the slip and in the cast ware. Depending on the outcome of such comparison, the next phase would be to determine the value of utilizing an exchange reaction as an aid to the casting mechanism for the reasons which have been stated.

III. Experimental Study

(1) Procedure

As a result of the foregoing discussion, an attempt was made to identify the form of clay obtained from the casting operation by means of a qualitative determination of the yield value of the cast specimen. The yield value was determined by using the torsion device developed by Norton[16] for the study and measurement of the plasticity of clays. A hollow cylindrical speci-

[14] E. A. Hauser and S. Hirshon, "Behavior of Colloidal Suspensions with Electrolytes," *Jour. Phys. Chem.*, **43**, 1015–36 (1939); *Ceram. Abs.*, **19** [6] 146 (1940).

* This reaction is more commonly known as "burning" a mold. A layer of calcium silicate ($CaSiO_3$) or calcium carbonate ($CaCO_3$) or both is deposited on the face of the mold which destroys its absorbent properties. A severe deposition of these insoluble reaction products may occur when an overdeflocculated slip is used, and a new mold can be "burned" in this case within one pouring.

[15] E. A. Hauser, "Colloid Chemistry in Ceramics," *Jour. Amer. Ceram. Soc.*, **24** [6] 179–89 (1941); see also reference 13.

† See references 9 and 12.

[16] F. H. Norton, "Instrument for Measuring Workability of Clays," *Jour. Amer. Ceram. Soc.*, **21** [1] 33–36 (1938).

men was cast in various molds according to tests to be outlined later, and a series of plaster and bisque molds was prepared for the work. The bisque molds were cast from a low-shrinkage body[17] and fired at 1010°C. to obtain high porosity and good strength. The low shrinkage of this body (1.5 to 2.0% total linear shrinkage) reduced to a minimum the difficulties usually experienced in the production of ceramic ware that requires close dimensional tolerances. The molds were soft enough after they were fired to permit machining so that cores could be fitted more exactly.

The casting slip (specific gravity at 1.80, corresponding to 26.75% of H_2O, wet basis) was prepared from a commercial sanitary-ware body according to specific directions,* and specimens were cast in the various molds after the proper period of aging. The moisture content within the cast specimen was allowed to equalize by aging for four days in an atmosphere saturated with water vapor. At the end of this period, the specimen was carefully mounted in the torsion apparatus, and a stress-strain diagram was obtained. Immediately after the test, a moisture determination was made on the sample.

A typical diagram obtained for clays or plastic ceramic bodies in torsion is shown in Fig. 2. An important feature of such a test is the absence of a sharp yield point. In order to obtain a relative yield value on such materials, various arbitrary methods have been in use.[18] The method adopted in this case, therefore, is justifiable, especially because the only aim has been to obtain comparative values relative to the form of clay existing in the cast. Figure 2 illustrates the method used to obtain the yield value. A line was drawn tangent to the initial slope of the stress-strain curve, and the intersection of this tangent (line *A*) with line *B*, which was extended from the portion of the curve with constant slope, was arbitrarily chosen as the yield value.

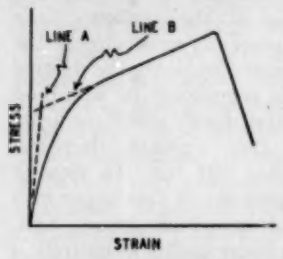

FIG. 2.—Typical stress-strain diagram obtained when testing cast specimens in torsion.

Yield-value determinations were made from samples cast (*a*) in plaster molds, (*b*) in bisque molds, (*c*) in bisque molds treated with a solution of calcium chloride, and (*d*) in bisque molds treated with aluminum chloride.

(2) Results

Reproductions of typical stress-strain diagrams obtained from the specimens cast in plaster molds are shown in Fig. 3 (*A*); those obtained using the bisque mold, the bisque mold treated with $CaCl_2$, and the bisque mold treated with $AlCl_3$ are shown, respectively, in (*B*), (*C*), and (*D*) of Fig. 3. Yield values were obtained from these diagrams and were tabulated with the percentage of water (wet basis) of the sample. From these data, curves showing the relation between the water content of the sample (wet basis) and the yield value are given in Figs. 4, 5, 6, and 7.

The results, in general, are those to be expected.[19] Curve *A* in Fig. 1, as stated previously, shows the relation between apparent viscosity and water content of the slip at the concentration of electrolyte used in these tests, and the viscosity values were observed to increase rapidly with small changes in the water content after a figure of 34% of water was reached. Curve *B* in Fig. 1 shows the relation between the yield value of the system and the percentage of water. The inflection in curve *A* could be interpreted as the point where the system changes from one with sufficient water yielding great mobility to one in which the water is distinctly limited to the quantity required to maintain a continuous phase.[13] Particle interference is to be anticipated in the latter case which results in

[17] F. H. Norton and G. Demetrios, "Art and Science in Sculpture," *Technology Rev.*, **44** [3] 120 (1942).

* The filter cake and deflocculent were supplied through the courtesy of the Universal Sanitary Mfg. Co. with complete directions for the preparation of the casting slip.

[18] I. H. Cowdrey and R. G. Adams, Materials Testing. John Wiley and Sons, Inc., New York, 1935.

[19] (*a*) A. V. Bleininger and D. W. Ross, "Flow of Clay Under Pressure," *Trans. Amer. Ceram. Soc.*, **16**, 392–400 (1914).

(*b*) R. T. Stull and P. V. Johnson, "Relation Between Moisture Content and Flow-Point Pressure of Plastic Clay," *Jour. Research Nat. Bur. Standards*, **22** [3] 329–37 (1939); R.P. 1186; *Ceram. Abs.*, **18** [6] 165 (1939).

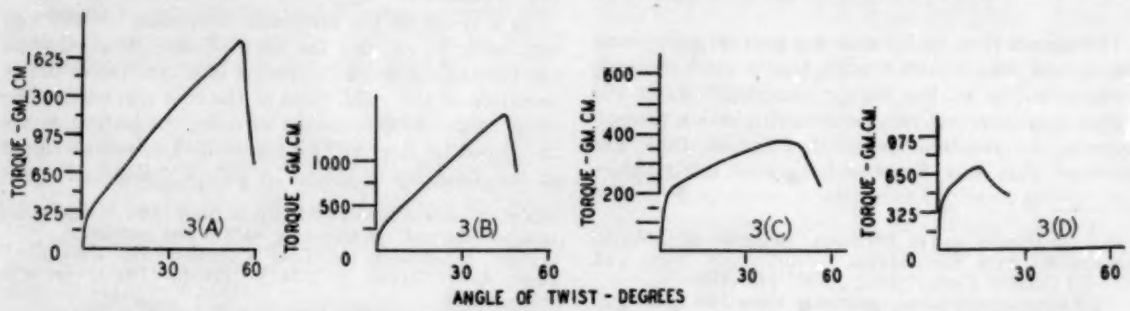

FIG. 3.—Typical stress-strain diagram of specimens cast as follows: 3 (*A*) in gypsum molds using regular commercial slip; 3 (*B*), in bisque molds using regular commercial slip; 3 (*C*), in bisque molds treated with calcium chloride using regular commercial slip; and 3 (*D*), in bisque molds treated with aluminum chloride using regular commercial slip.

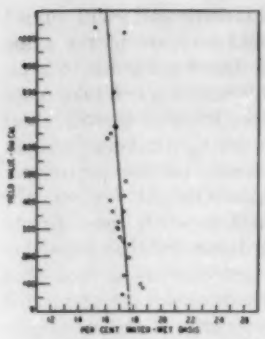

FIG. 4.—Relation between yield value and percentage of water on specimens cast in gypsum molds using regular commercial slip.

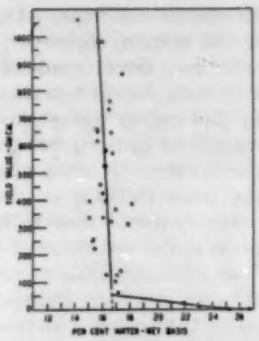

FIG. 5.—Relation between yield value and percentage of water on specimens cast in bisque molds using regular commercial slip.

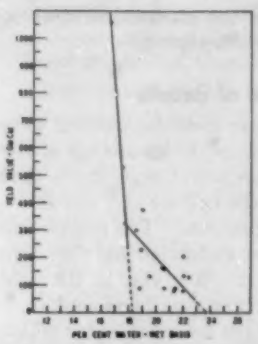

FIG. 6.—Relation between yield value and percentage of water on specimens cast in bisque molds treated with calcium chloride using regular commercial slip.

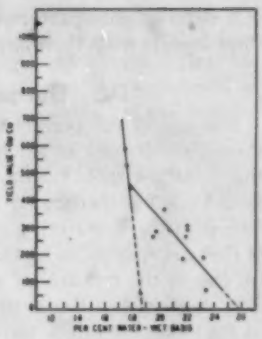

FIG. 7.—Relation between yield value and percentage of water on specimens cast in bisque molds treated with aluminum chloride using regular commercial slip.

high viscosity values. With additional dewatering, a point is reached wherein the system ceases to have water as the continuous phase. The viscosity of the system, however, becomes meaningless in this condition, and to evaluate the rigidity, the yield value gives a more accurate description. The inflection point in plotting yield value versus water content would indicate such a region. Curve *B* in Fig. 1, for example, shows no such inflection for the yield values obtained on the system down to 22% of water; Fig. 5, however, indicates that the system changes thus at about 17% of water. The data shown in Figs. 1 and 5 have been compared because casting by means of the bisque mold should be simply a dewatering operation and no change in the clay form should occur. The yield value of the slip at the several water contents shown in Fig. 1 was determined by means of the modified MacMichael viscosimeter.[20]

The combined results of Figs. 1 and 5 show that to obtain a cast the clay–water system must exhibit a yield value of between 50 and 100 gm. cm., which occurs at a water content of approximately 17% for the clay OH–Na system. It may also be stated that, in the clay OH–Na system at 17% of water, the system changes to one in which water is no longer the continuous phase. The results shown in Fig. 4, where casts were obtained from the plaster molds, indicate that a water content of about 17% is also needed before the yield value of the clay–water system is high enough to permit successful casting. The mechanism of casting, therefore, must be the same in these two instances, inasmuch as a change in the form of the clay should be indicated by varying the percentage of water at which the clay–water system transforms itself from the rigid to the mobile state[13] (as will be explained later).

A different type of result is obtained with bisque molds which have been treated with calcium and aluminum chloride. In these systems in the region where water is still the continuous phase (between 18 and 23% in Fig. 6 and between 18 and 25% in Fig. 7) and where the viscosity would be expected to increase rapidly, the yield value of the system is sufficiently high to permit casting. The results in Figs. 6 and 7 show that the yield value in this area changes slowly with decreasing concentrations of water down to about 18% (wet basis). A relatively safe casting range with a wide variation of water content is therefore provided wherein the casting proceeds at a rate that is not too rapid to make the manipulations critical. The cores, for example, may be pulled or a mold may be opened and the cast removed without difficulty at a water content of 23% or at 18% (see Fig. 7). The removal of 5% of water by a porous mold requires time, and this value, translated into increased tolerances in timing industrial casting operations, merits attention. The results on tests using the treated molds show furthermore that at approximately 18% of water on the wet basis both systems pass into the form where water is no longer the continuous phase. This result, however, is not fully in accord with the theory that different forms of clay would show this inflection in the yield value of the system at various water contents. The fact that chlorides were used in both cases would possibly have a bearing on this result.

Although most of the results shown in Figs. 1, 4, 5, 6, and 7 represent consistent data, those in Fig. 5 tend to be erratic and require some explanation. One kilogram of slip was prepared at a time, and at least three specimens in each type of mold were cast from this batch. This procedure required the preparation of several batches of slip with the possibility of variation between batches. The variation may be attributed to slight changes in the electrolyte content which effect a marked change in the properties of a slip. The amount of electrolyte present in the slip would thus affect the properties of a cast produced by the dewatering mechanism to a greater extent. The wider divergence in the results shown in Fig. 5, where casts from the bisque molds were obtained by dewatering, may be explained in part by this reasoning.

[20] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: I, Preparation of Purified Kaolinite Suspension," *Jour. Amer. Ceram. Soc.*, **24** [2] 64–69 (1941).

A detailed interpretation of the phenomena causing these results may therefore be attempted.

IV. Discussion of Results

The use of the porous bisque mold for casting ware should result only in the mechanical dewatering of the slip. Such a mold contains no active ingredients that would react with the clay of the casting slip and interfere with the dewatering mechanism. The production of the cast specimens by this procedure should therefore be due to the removal of water. The clay in the final cast should be in the same chemical and colloidal state as that existing in the slip except for some water which has been absorbed by the mold. In order to cast ware successfully by means of dewatering a deflocculated casting slip, the water content of the slip must be reduced from the original value (26.75% in this case) to at least 17% (wet basis) according to the results shown in Fig. 5. This value is equivalent to an increase in the specific gravity value of the slip from the original 1.80 to about 2.00. At such density, the clay–water system displays a yield value sufficient to give the required rigidity for handling; at lower densities, the system is too fluid to remove the cast from the mold.

The results obtained from the bisque molds treated with $CaCl_2$ and $AlCl_3$ solutions are substantially different (Figs. 6 and 7). In the first place, casts may be obtained at a higher water content and over a wider range than is possible with the porous bisque mold. The yield point of the original slip dewatered to a value of 22% of water, for example, was determined in a viscosimeter, whereas a cast was obtained at this moisture content when the treated molds were used. Some change in the system obviously has occurred to permit casting at such water content. According to Fig. 5, which shows the relation between yield value and water content for the clay OH–Na system, the clay form in the casts obtained with the molds treated with $CaCl_2$ and $AlCl_3$ is not clay OH–Na although this form of clay was introduced as the slip. Theoretically, the following reactions between the slip and the treated molds may occur:

$$2[\text{Clay OH–Na}] + Na_2SiO_3 + 2CaCl_2 \longrightarrow (\text{clay } OH)_2Ca + 4NaCl + CaSiO_3. \quad (5a)$$

$$2[\text{Clay OH–Na}] + Na_2CO_3 + 2CaCl_2 \longrightarrow (\text{clay } OH)_2Ca + 4NaCl + CaCO_3. \quad (5b)$$

The calcium or aluminum chloride of the mold would first neutralize the excess sodium silicate or carbonate; then, if sufficient Ca^{++} or Al^{+++} ions were available, an exchange reaction with the clay OH–Na would occur causing the formation of the (clay $OH)_2Ca$ or (clay $OH)_3Al$ according to equations (5). The properties of a clay–water system containing (clay $OH)_2Ca$ or (clay $OH)_3Al$ are different from those of the system containing clay OH–Na. In the first place, the zeta potential of the particle decreases in the order of Na^+, Ca^{++}, Al^{+++} to H^+. It has been shown* that the viscosity of a clay–water system increases with decreasing zeta potential on the particle if all other factors are constant. The plasticity and yield value* of the system, moreover, would increase in the same order as a direct result of the decreased value of zeta. This reduction in zeta shows why casting can take place in this region where the water content is still great enough to cause water to be the continuous phase in the system. With a reduced zeta on the particle in the (clay $OH)_2Ca$ or the (clay $OH)_3Al$ system, the particles would tend to be held together more firmly because the reduction of zeta indicates that repulsion forces (attributable to zeta) are decreasing and that the resultant force changes, which causes the attraction forces to increase. In this same range of water content, the clay OH–Na system exhibits high viscosity values because of particle interference; the zeta potential, however, is so great that repulsion forces predominate, and the system displays a certain amount of mobility.

An analysis of the data obtained using the gypsum mold (Fig. 4) shows that dewatering is the principal mechanism of casting in this case. As has been pointed out, the calcium sulfate of the mold should react with the deflocculated slip according to reactions 6(*a*) and 6(*b*).

$$Na_2SiO_3 + 2[\text{clay OH–Na}] + CaSO_4 \longrightarrow (\text{clay } OH)_2Ca + Na_2SO_4 + CaSiO_3. \quad (6a)$$

$$Na_2CO_3 + 2[\text{clay OH–Na}] + CaSO_4 \longrightarrow (\text{clay } OH)_2Ca + Na_2SO_4 + CaCO_3. \quad (6b)$$

Equations (6) show that the (clay $OH)_2Ca$ form should have been produced and that casting results should have been observed similar to those obtained from the bisque mold treated with calcium chloride. The data shown in Fig. 4, however, do not compare favorably with those of Fig. 6, and some explanation is required. Equation (1) (p. 338), which gave the reaction between commercial clays and the deflocculents used in preparing the casting slip, shows that if soluble salts exist in the form of sulfates this ion will be present in the final slip in the sodium sulfate (Na_2SO_4) form unless steps are taken for its removal. The presence of the sulfate radicle, therefore, can interfere with the dissociation of the calcium sulfate of the mold by the common ion effect. According to calculations, the presence of 0.07% of sodium sulfate on dry body basis per liter of slip at 1.80 specific gravity would be sufficient to suppress the ionization of the calcium sulfate of the mold entirely and thereby shut off the supply of Ca^{++} ions which are needed to cause the exchange reaction between the clay and the mold. A comparison of the results shown in Fig. 4 with those of Fig. 5 indicate that no exchange reaction occurs and that the plaster mold functions only as an absorber. The casting mechanism in this case is one of mechanical water absorption, probably due to the presence of the interfering sulfate ion.

It has been stated previously that treatment of a slip containing sulfates with barium carbonate ($BaCO_3$) would render this ion insoluble and have the effect of removing it from the system† (see also equation (2), p. 338). Although this theory appears to be a solution

* See reference 13, p. 338 and reference 15, p. 339.

† See references 9 and 11, p. 338.

to the problem, a more careful analysis indicates that this is not the case. The product of the reaction between the calcium sulfate of the mold and the sodium salts used as deflocculents in a sulfate-free slip, according to equations (6), is additional sodium sulfate. This would be true if the excess electrolyte were the first to react (which appears likely); the formation of sodium sulfate by this reaction would thus cause the ionization of the calcium sulfate to cease as soon as the concentration of the sulfate ion equals the square root of the solubility product for calcium sulfate. If the reaction between the calcium sulfate of the mold and the clay OH–Na of the sulfate-free slip were to take precedence over the reaction between the mold and the excess deflocculents, sodium sulfate would still be the by-product. The ionization of the Ca^{++} ions furnished by the plaster mold would also cease as soon as the value of the solubility product were exceeded. It can be shown by calculations, however, that this exchange reaction would transform only about one third of the clay OH–Na present in the slip to the desired (clay OH)$_2$Ca form. The results on a series of tests, in which barium carbonate-treated slips and plaster molds were used, thus indicate that insufficient transformation of the clay OH–Na to (clay OH)$_2$Ca has taken place.

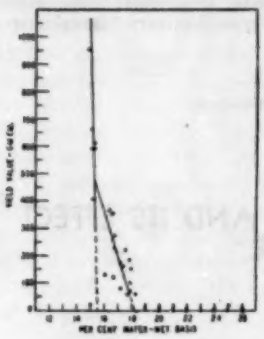

FIG. 8.—Relation between yield value and percentage of water in specimens cast in gypsum molds using barium carbonate-treated slip.

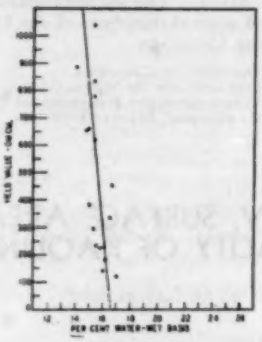

FIG. 9.—Relation between yield value and percentage of water on specimens cast in bisque molds using barium carbonate treated slip.

Figure 8 shows the relation of yield value versus water content in the casting range when the sulfate-free slips and plaster molds are used. Figure 9 shows the same relation with bisque molds. A comparison of the results in Figs. 4 and 8 shows that the casting mechanism in the latter case is something more than the removal of water and that alteration in the form of clay is taking place. The results, however, using the mold treated with calcium chloride (Fig. 6), indicate the ultimate to be expected with the Ca^{++} ion.

V. Practical Considerations

Aside from the theoretical significance of casting by an exchange reaction, the process described merits practical consideration. The processes used in the manufacture of ceramic ware, which depends on the plasticity of clays, may be divided into two main classifications, namely, plastic forming and slip forming. The first method requires the plastic type of clay which occurs abundantly in nature, and the user need only select a clay to his liking, compound a proper body, and temper the mixture with water before the forming operation. The use of clay in the second operation is a new method which has slowly developed into a scientific process and which ranks high among chemical and colloidal phenomena. The primary purpose of the present-day casting slip is to increase its pouring qualities, probably at the expense of the working properties which emerge after the ware has been formed. The pioneers who envisaged the casting process never thought that the complicated shapes, which today are being cast separately and then stuck together, would be a result of this process. This sticking operation requires that the casts have the good working properties usually present in the clay employed for plastic forming operations. The same body will be used occasionally for the fabrication of ware both by plastic and casting methods. The workability and plasticity of the body as it is compounded from natural clay is well suited for use in the plastic forming method; in the preparation of the casting slip, however, the introduction of deflocculents changes the form of clay into a less plastic state. If the users of the casting process could first, by some manipulation, utilize the excellent properties of the clay OH–Na form for pouring slip and then revert to the more plastic and workable (clay OH)$_2$Ca form for the subsequent operations, the difficulties and limitations connected with the casting process would be somewhat reduced. From this viewpoint, casting by the exchange reaction has possibilities worthy of additional research.

TABLE II

CASTING RANGE DATA

Clay form	Type of mold	Range (%)	Minimum dewatering (%)
Clay OH–Na	Plaster	3	8
Clay OH–Na	Bisque	3	8
(Clay OH)$_2$Ca	$CaCl_2$ bisque	7	4
(Clay OH)$_3$Al	$AlCl_3$ bisque	8	3

Aside from the improvement in working properties of a cast formed by an exchange reaction, the casting range is considerably longer by this process. Table II indicates the casting range in water content of the cast on the wet basis, and it also shows the minimum amount of water which must be absorbed by each type of mold before a cast can be obtained using normal casting times. The increased range in percentage of water of the cast translated into time indicates that timed casting operations may have greater latitude, and the procedure followed in the experimental work bears out this fact. Using the plaster mold, the core was pulled between 13 and 15 minutes after the mold was filled, and 5 minutes after the core was pulled the mold was opened. This timetable had to be followed to obtain satisfactory casts. In the case of the treated bisque molds, the cores could be pulled and the mold opened almost simultaneously, and the casting time

could be varied from 10 or 15 minutes to three quarters of an hour, depending on the condition of the mold.

It should be possible, theoretically, to cast ware without dewatering the slip if the original density of the slip is properly adjusted beforehand and if sufficient time is allowed for the complete conversion of the clay OH–Na to any form of lower zeta. Figure 7 shows that casting could take place with no dewatering, by preparing the slip at 25% of water (1.83 specific gravity) and by using molds treated with aluminum chloride. The same result, according to Fig. 6, could be obtained with molds treated with calcium chloride and a slip with a water content of 23% (1.88 specific gravity); at this water content and after conversion to the (clay OH)$_2$Ca form, the clay has sufficient yield value to allow handling. From a practical standpoint, the reason for casting with no water removal whatever is that no volume change occurs in such a casting mechanism, which eliminates the shrinkage problems connected with the casting process. Inasmuch as shrinkage of the cast occurs only during the drying operation, there would be no shrinkage of the cast in the mold if there were no dewatering of the cast. Casting by a combination of an exchange reaction and some dewatering, on the other hand, offers no serious difficulty and could be easily carried out.

Additional investigation for the best mold that would be suitable for casting by an exchange reaction will have to be undertaken, especially if this process is to be adapted for commercial use. Bisque molds are not entirely eliminated because the necessary porosity and strength can be attained by the selection of low-shrinkage bodies[17] and by proper firing. It may be possible also to treat plaster molds so that they could be utilized for casting by this new mechanism.

VI. Conclusions

The following conclusions based on this work appear logical:

(1) Casting ceramic ware by means of deflocculated slips and plaster of Paris molds ($CaSO_4$) is essentially a process whereby the slip is dewatered by the porous mold. The cast contains clay substantially in the same colloidal form as that introduced with the slip.

(2) By the selection of the proper mold, which allows the Na^+ ion of the clay to be exchanged for any di- or tri-valent cation or hydrogen, the properties of the system are altered in such manner as to constitute a casting mechanism.

(3) Casting by a combination of the dewatering and exchange processes may also be utilized.

Acknowledgment

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Division of Ceramics
Department of Metallurgy
Massachusetts Institute of Technology
Cambridge, Massachusetts

FUNDAMENTAL STUDY OF CLAY: IV, SURFACE AREA AND ITS EFFECT ON EXCHANGE CAPACITY OF KAOLINITE*

By A. L. Johnson and W. G. Lawrence†

Abstract

Six monodisperse fractions of kaolinite were prepared, and the exchange capacity was determined from the viscosity relations on additions of NaOH to the electrodialyzed fractions. A linear relationship is shown to exist between the surface area and the base-exchange capacity for all of the sizes studied.

I. Introduction

The exchange capacity of kaolinite varies, depending on the surface area of the sample.[1] Speil[2] has shown a linear relation to exist between exchange capacity and surface area for three monodisperse fractions of kaolinite. Harman and Fraulini[3] also describe a linear relation in the smaller size range, but their results show abnormally high capacity values for the coarser size of particles, which was attributed to the greater surface area of the "booklike" formations in the coarser particles.

With an improved technique and data for the preparation of purified kaolinite,[4] the present object was to determine the exchange capacity of six closely monodisperse fractions of kaolinite prepared from Florida clay.

II. Experimental Procedure

The monodisperse fractions of kaolinite were pre-

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942 (White Wares Division). Received May 6, 1942.

† This paper was prepared from material from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Science, Massachusetts Institute of Technology, Cambridge, Mass.

[1] R. E. Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939).

[2] S. Speil, "Effect of Adsorbed Electrolytes on Properties of Monodisperse Clay–Water Systems," *ibid.*, **23** [2] 33–38 (1940).

[3] C. G. Harman and Felix Fraulini, "Properties of Kaolinite as Function of Its Particle Size," *ibid.*, **23** [9] 252–59 (1940).

[4] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: I, Preparation of a Purified Kaolinite Suspension," *ibid.*, **24** [2] 64–69 (1941).

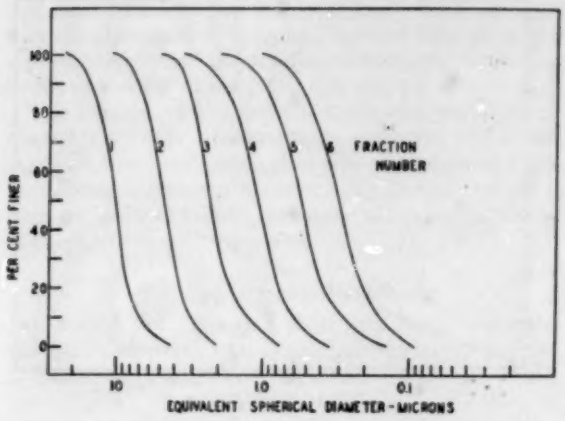

FIG. 1.—Accumulative particle distribution of six closely monodisperse systems prepared from Florida clay.

pared according to the method outlined by Norton and Speil,[5] and the particle-size distribution of the fractions was determined by the hydrometer method,[6] using a long arm centrifuge. The distribution of sizes in the coarse fractions (Nos. 1 and 2) was determined by microscopic count. Figure 1 shows the accumulative particle distribution of the fractions used. From data given in Fig. 1, a value of size was obtained for each fraction which represented the diameter occurring most frequently and which could be taken as the representative size for the particular fraction under consideration. This value is listed in Table I as the calculated value of the mean particle size. Photographs of fractions Nos. 3 to 6, inclusive, taken by means of the electron microscope, made possible a check on the size of the particles as determined by Stokes' law. These observations indicated agreement between the diameter as calculated from Stokes' law and the largest dimension of the particle (Table I).

TABLE I

Fraction No.	Mean particle size (μ) Observed	Calculated	Specific surface (sq. m./gm.)	Exchange capacity (m.e. NaOH/ 100 gm.)
1	10.0	10.0	1.1	0.4
2	4.4	4.4	2.5	0.6
3	1.8	2.5	4.5	1.0
4	1.2	0.95	11.7	2.3
5	0.56	0.52	21.4	4.4
6	0.29	0.28	39.8	8.1

After preparation, each fraction was treated to remove organic matter and soluble salts according to the method outlined in Part I.[4] The sample was finally electrodialyzed to obtain the clay OH–H form, and viscosity relations were made on sodium hydroxide (NaOH) additions. The electrodialyzed samples for this test were made up to 16% by weight of clay with the proper NaOH content. The suspensions were

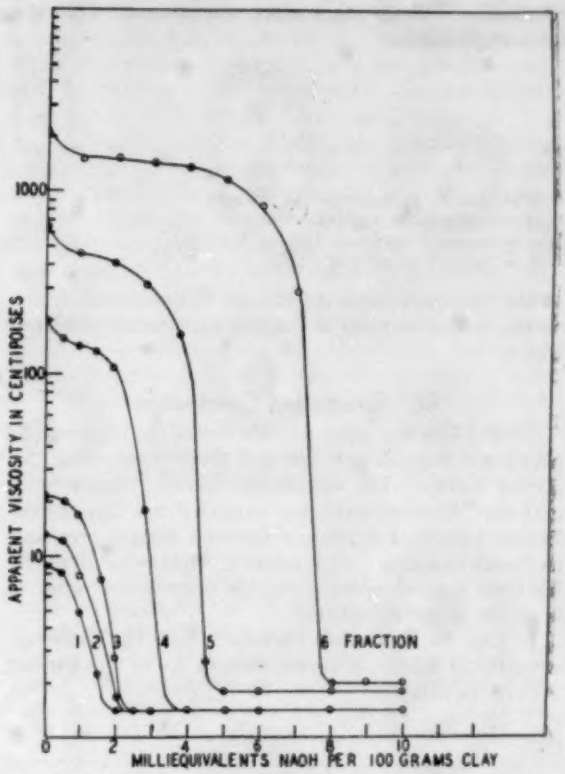

FIG. 2.—Viscosity relations on sodium hydroxide additions to electrodialyzed monodisperse fractions.

placed in glass-stoppered bottles, agitated for 24 hours, aged for a similar period, and deaired. The viscosity values were then determined with a MacMichael viscosimeter.[4] Figure 2 shows the type of data obtained on the several fractions and represents data on at least two series of determinations.

The mineralogical composition of each fraction was determined by X-ray[*] and thermal[7] analyses. These observations indicated that the samples were substantially 100% kaolinite.

In calculating the surface area of the fractions, an assumed ratio of the thickness to the diameter or length of the particle is necessary. Whittaker[8] used a ratio of 0.08, based on ultramicroscopic studies of clay. Observations made with the electron microscope using fraction No. 6 indicate that the particle thickness is approximately 200 a.u. (0.02 μ). The mean diameter of the fraction from the particle-size data appears to be about 0.28 μ. The ratio of 0.08 used by Whittaker[8] to calculate the surface area is therefore a fair approximation and was used in the present study. It is not known definitely whether this ratio holds for all sizes; this assumption is made, however, for the purpose of cal-

[5] F. H. Norton, and S. Speil, "Fractionation of a Clay into Closely Monodispersed Systems," *Jour. Amer. Ceram. Soc.*, 21 [10] 367–70 (1938).

[6] F. H. Norton and S. Speil, "Measurement of Particle Sizes in Clays," *ibid.*, 21 [3] 89–97 (1938).

[*] The X-ray analysis was made by J. Biscoe, Department of Physics, Massachusetts Institute of Technology.

[7] F. H. Norton, "Critical Study of Differential Thermal Method for Identification of Clay Minerals," *Jour. Amer. Ceram. Soc.*, 22 [2] 54–63 (1939).

[8] H. Whittaker, "Effect of Particle Size on Plasticity of Kaolinite," *ibid.*, 22 [1] 16–23 (1939).

culations. The specific surface was obtained from the following formula:

$$S = \frac{2(1 + 2x)}{\rho D x}$$

$$S = \frac{11.15}{D}$$

S = specific surface/gm. of sample.
D = mean diameter (μ).
x = ratio of thickness to length (0.08).
ρ = density of sample (2.62).

The exchange capacity of each fraction was taken as the inflection point in the viscosity curves shown in Fig. 2.

III. Results and Conclusions

Table I lists the mean particle size of each fraction as calculated from Stokes' law and the corresponding observed values. The calculated specific surface area and the observed exchange capacity are also listed. Figure 3 shows the relation between surface area and exchange capacity. This relation is linear for all of the fractions studied, which cover the particle-size range of kaolinite rather completely.

It may be concluded, therefore, that the exchange capacity of kaolinite varies directly as to the surface area of the sample.

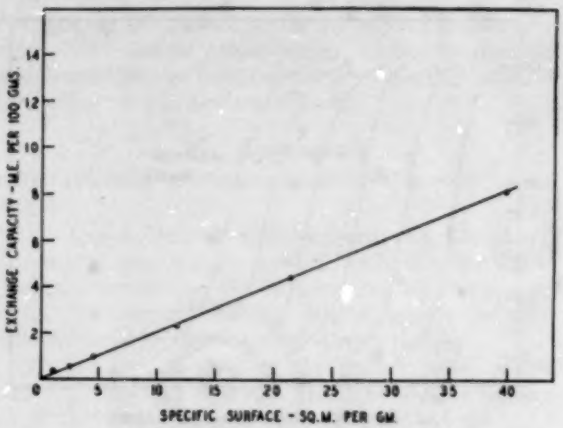

FIG. 3.—Relation between specific surface per gram of kaolinite and exchange capacity per 100 grams.

Acknowledgment

The authors wish to acknowledge the cooperation of G. G. Harvey and L. J. Sullivan of the Department of Physics, in connection with the observations made by means of the electron microscope, and to F. H. Norton for his interest and criticism during the study.

DEPARTMENT OF METALLURGY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

EFFECT OF STEAM AND HOT WATER WITH SODA ASH AND A WETTING AGENT ON PROPERTIES OF CLAY*

BY H. G. SCHURECHT, J. F. MCMAHON, AND C. M. LAMPMAN

ABSTRACT

The use of combined treatments was found to be more efficient in improving the properties of clays than individual treatments, and the best results were obtained when the clay was pugged with steam and hot water with an addition of 0.2% of soda ash. This process lowered the water of plasticity 26%, the drying shrinkage 58%, and the absorption 46.5%. The dry and fired strengths were increased 123% and 144%, respectively.

I. Introduction

With specifications for heavy clayware becoming more rigid from time to time, the clayware manufacturers are constantly required to improve the quality of their products. Various additions and methods of preparing clays are known to affect their properties, but information on the influence of these methods has not been available, especially on tests relating to combinations of these treatments.

The addition of small amounts of an electrolyte, such as soda ash, to clays has been shown[1] to increase the dry strength more than 100% and the fired strength more than 50%. Hot water has been used in pugging clays to improve their extrusion behavior, but there is little information on the effect of hot or cold water on the other properties of the clay body.

Preliminary tests showed that a 1-in. cube of dried clay disintegrates about three times as fast in water at 70°C. as it does as 4°C. The introduction of steam in the pugging and deairing chambers of an extrusion machine, moreover, not only heats the clay but replaces the air in contact with the clay during pugging, thus deairing it to a certain extent. The deairing of

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Structural Clay Products Division). Received March 3, 1942.

[1] (*a*) H. G. Schurecht, "Effect of Electrolytes on Some Properties of Clays," *Jour. Amer. Ceram. Soc.*, **1** [3] 201–13 (1918).
(*b*) G. J. Barker and Emil Truog, "Improvements of Stiff-Mud Clays Through pH Control," *ibid.*, **21** [9] 324–29 (1938).

stiff-mud bodies is known to increase their strength and to reduce their absorption, but few data are available on the effect of the deairing process when it is combined with some of the other clay treatments.

The purpose of the present study was to determine the influence of hot water, steam, soda ash, and a wetting agent on a clay when each was used alone and also in combined treatments. Unusually great increases in strength were obtained, especially when combinations of these treatments were used.

II. Experimental Methods

A New York Chemung shale was used, which had the following screen analysis: >20-mesh, 13%; 20- to 28-mesh, 15%; 28- to 35-mesh, 10.1%; 35- to 48-mesh, 7.6%; 48- to 65-mesh, 6.7%; 65- to 100-mesh, 5.9%; and <100-mesh, 41.4%.

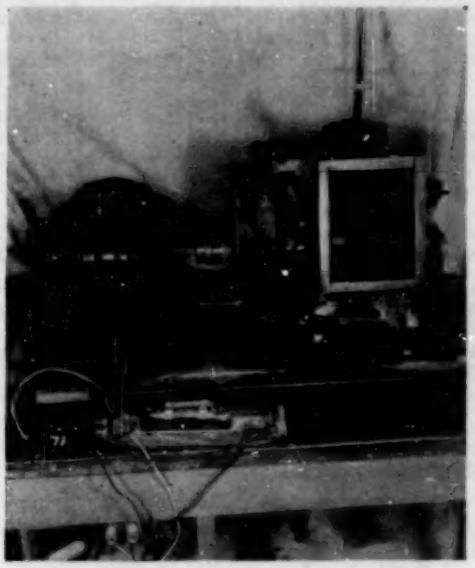

FIG. 1.—Read mixer used to pug the clay.

A Readco laboratory mixer* was used, which was so equipped that pugging could be carried out under vacuum as well as at atmospheric pressure (Fig. 1). It was also fitted with a steam jacket to permit the batch to be pugged under hot and cold conditions.

(1) Pugging Treatments

The following pugging treatments were used: (*a*) With no addition, (*b*) combined with the addition of 0.2% of soda ash in terms of dry clay, and (*c*) combined with 0.2% of wetting agent in terms of total water content. The soda ash and wetting agent were added as solutions.

(*A*) *Normal Pugging:* Pugging was continued for 20 minutes after a predetermined amount of water, that is, enough to produce maximum plasticity, was added to the dry shale.

(*B*) *Pugging Under Vacuum:* The charge was placed in the chamber and closed with an airtight cover; it was then evacuated, the desired amount of water was introduced through an opening in the cover, and the batches were pugged for 20 minutes under a vacuum of 12.5 in. and 25.0 in., respectively.

(*C*) *Pugging with Hot Water:* The pugging chamber was preheated by passing steam through the jacket, the charge was introduced, and the cover was clamped in place. The clay was allowed to remain in the machine for 5 minutes to heat the clay, boiling water was added, and the batch was pugged for 20 minutes.

(*D*) *Pugging with Steam and Hot Water:* The pugging chamber was preheated as in treatment (*C*), and the mill was run for 5 minutes to heat the dry-ground shale. Steam at 1 lb. of pressure was introduced in the chamber for 2 minutes. Because the water condensed from the steam was insufficient to produce the necessary plasticity, boiling water was added to make up the difference. Pugging was continued for 20 minutes after the water was added.

(2) Tests

Tests were conducted on each batch to determine (1) water of plasticity, (2) drying shrinkage, (3) ratio of percentage of shrinkage to that of water of plasticity, (4) dry bulk density, (5) dry transverse strength, (6) fired volume shrinkage, (7) absorption, (8) fired transverse strength, and (9) fired bulk density. The absorption determinations were made after the specimens were boiled in water for 2 hours.

III. Discussion of Results

The influence of various treatments on the properties of New York shale are shown in Table I and in Figs. 2, 3, and 4. Table II shows the relative effect in percentage of decrease or increase caused by eleven different test treatments.

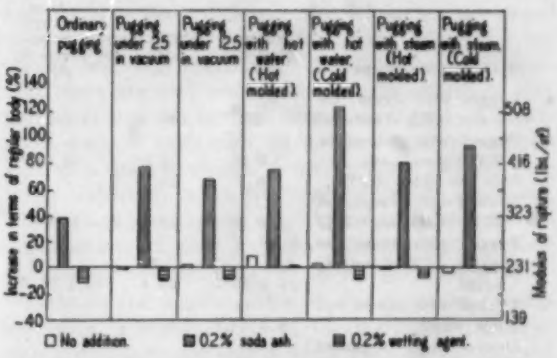

FIG. 2.—Effect of treatments on dry strength of New York shale.

When hot water or steam was used in the tests for water of plasticity, different results were obtained on the hot-molded and cold-molded specimens; for this reason, only maximum and minimum percentage changes are given. In the tests in which cold molding alone was employed, only one percentage change is given for each treatment.

It is apparent that the combined treatments

* Read Machinery Co., Inc., York, Pa.

TABLE I

INFLUENCE OF VARIOUS TREATMENTS ON PROPERTIES OF NEW YORK SHALE

Additions*	Water of plasticity (%)	Dry shrinkage (%)	Ratio of shrinkage to water (%)	Dry density	Dry modulus of rupture (lb./in.²)	Fired vol. shrinkage (%) Cone No.			Water absorption after boiling 2 hr. (%) Cone No.			Fired modulus of rupture (lb./in.²) Cone No.			Fired density Cone No.		
						09	05	03	09	05	03	09	05	03	09	05	03
Ordinary pugging																	
A	19.2	11.8	0.61	2.06	231	2.5	5.0	7.0	14.1	13.1	10.5	517	1203	2445	1.87		2.01
B	16.1	9.9	0.61	2.10	319	1.7	3.8	5.9	12.0	10.9	7.9	842	1954	2571	1.96	2.07	2.10
C	17.5	9.6	0.55	2.03	204	0.8	5.3	8.5	14.1	13.2	9.3	600	1460	1950	1.89	2.02	2.10
Pugging under 25 in. of vacuum																	
A	18.6	9.9	0.53	2.05	229	1.1	5.3	7.4	13.7	12.7	10.0	639	1653	2194	1.91	2.04	2.02
B	16.2	9.1	0.53	2.09	409	1.2	5.5	5.7	12.4	10.2	8.6	942	2302	3117	1.95		2.17
C	17.3	7.3	0.42	2.01	207	2.3	6.7	7.5	14.1	12.3	9.9	601	1508	2185	1.90		2.06
Pugging under 12½ in. of vacuum																	
A	19.0	10.8	0.57	2.02	238	0.5	5.8	7.4	14.2	13.2	9.2	687	1629	2418	1.88	2.02	2.06
B	15.6	7.8	0.50	2.10	385	0.7	6.8	7.6	12.0	10.3	7.5	900	1945	2961	1.98	2.10	2.14
C	17.4	6.2	0.36	2.00	207	1.3	5.4	6.8	14.3	11.9	10.0	534	1166	2217	1.90		2.04
Pugging with hot water (hot molding)																	
A	17.5	10.0	0.57	2.08	250	0.0	4.4	5.3	13.3	11.8	8.9	625	1407		1.94	2.07	2.13
B	16.3				404					9.34		808					
C	18.2	6.8	0.37	2.07	232	1.3	3.2	6.9	13.2	11.2	9.8	463		1744	1.97	2.06	2.07
Pugging with hot water (cold molding)																	
A	18.3	10.7	0.59	2.04	237	0.8	3.9	5.7	13.7	12.2	9.3	490	1569		1.94	2.02	2.08
B	14.2	6.6	0.46	2.17	515	0.4	5.9	6.5	10.3	8.9	6.4	1060	2595		2.04	2.19	2.19
C	18.7			2.03	208	1.3	4.9	5.7	13.7	12.1	9.8	463	1627	2009	1.90		2.05
Pugging with steam (hot molding)																	
A	17.6	10.9	0.62	2.09	224	1.8		3.8	13.3	11.7	9.8	472		2038	1.91		2.07
B	14.3	7.0	0.49	2.13	417	0.3	5.7		10.7	7.0	5.6	853		2329	2.06	2.18	2.23
C	16.6	8.8	0.53	2.09	213	0.9		5.8	13.8	11.7		541			1.95	2.09	2.11
Pugging with steam (cold molding)																	
A	16.6	8.5	0.51	2.04	220	2.2		5.3	12.8	11.2	10.1	528	1779	2023	1.92		2.04
B	14.2	5.5	0.39	2.15	445	1.0	5.0	7.6	10.5	7.6	6.5	1113	2929	3358	2.05	2.15	2.20
C	16.8	8.8	0.48	2.06	227	2.1	5.0	7.9	13.0	11.9	9.1	688	1539	2345	1.91	2.06	2.10

* A, no addition; B, soda ash, 0.2%; C, wetting agent, 0.2%.

TABLE II

RELATIVE EFFECT OF DIFFERENT TREATMENTS ON VARIOUS PROPERTIES OF FIRED SHALE*

Method of treatment	Water of plasticity (1)	Shrinkage (dry) (2)	Ratio of shrinkage to water of plasticity (3)	Density (dry) (4)	Strength (dry) (5)	Shrinkage (fired) (6)	Absorption (fired) (7)	Density (fired) (8)	Strength (fired) (9)
1. Pugged with steam, hot water, 0.2% of soda ash	26	40–58	19.7–36.1	3.4–4.2	80.6–92.7		24.1–46.5	10–11	38–144
2. Pugged with hot water, 0.2% of soda ash	15–26	32.6	32.6	5.3	123		27–39	9	105–116
3. Soda ash added (0.2%)	16.1	16.2		1.9	38.1	15.7–24.0	14.9–24.9	4.5	5–39
4. Deaired under vacuum of 25 in. (soda ash, 0.2%)	15.7	23.0	13.1		77.1		12.1–22.3	4.3–5.5	27.5–91.7
5. Pugged with steam, hot water, 0.2% of wetting agent	14.3–15.7	25.4	13.1–21.3	15–1.5	0		2.1–13.4	2.0–5.3	4.5–33
6. Pugged with steam and hot water	8.3–13.6	7.6–28				24.3–45.8	2.8–14.5		48
7. Deaired under vacuum of 25 in., 0.2% of wetting agent	10	38.3	31.2				5.7–6.1	1.7–2.5	16.3–25.7
8. Pugged with hot water	4.7–8.9	9.3–15.3			2.5–7.6	12.0–24.3† 18.6–22.0‡	3–15	3.4–5.6	14.5–23.3
9. Wetting agent added (0.2%)	8.8	10.2	9.8					1–4	16.3–21.4
10. Pugged with hot water, 0.2% of wetting agent	2.6–5.2					18.6		1.6–5.3† 1.5–3.0‡	31–35
11. Deaired under 25 in. of vacuum	3.3	16.1	13.1	1.5			2.9–3.9	2–3	23.6–37.4

* Columns (1), (2), (3), (6), and (7) show percentage of decrease; columns (4), (5), (8), and (9) show percentage of increase.
† Hot-molded process.
‡ Cold-molded process.

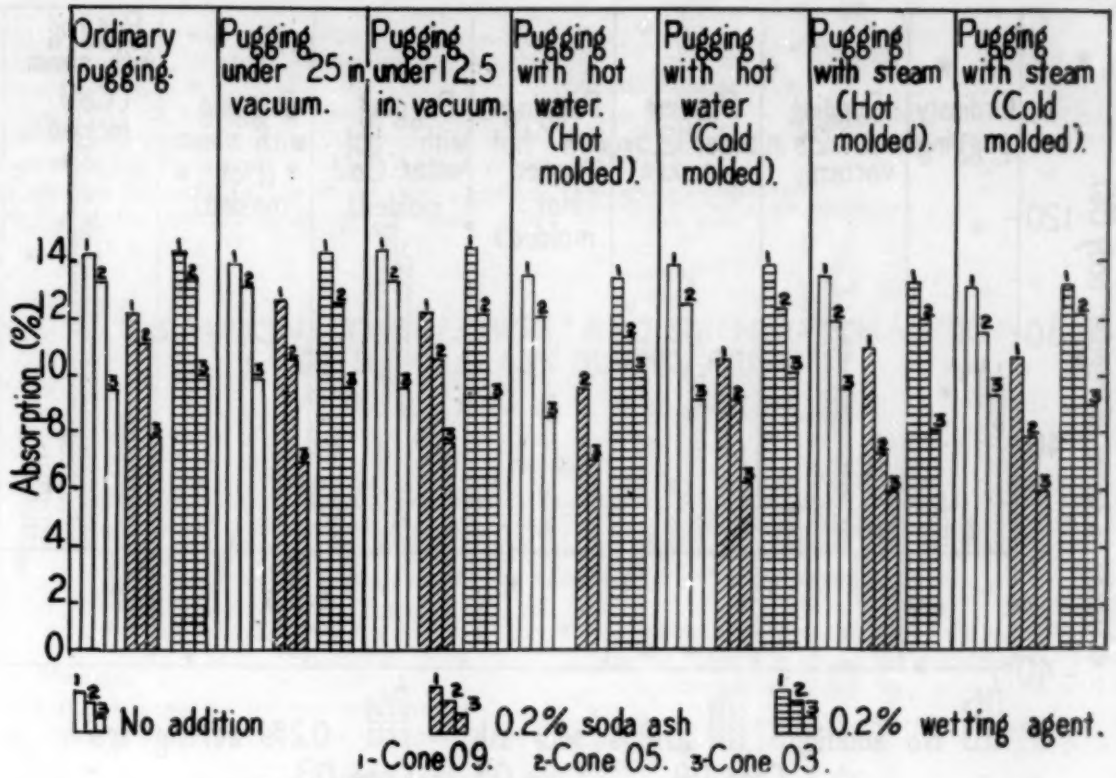

FIG. 3—Effect of treatments on absorption of New York shale.

decreased the water content more effectively than the individual treatments, although all of them decreased the water of plasticity lowered the drying costs. In some cases, the clay treatment effected a 26% reduction in the amount of water to be driven off in the drier.

The combined treatments were also effective in reducing the amount of shrinkage. The use of steam and hot water in pugging ranked first in effecting this decrease in shrinkage, and good results were obtained also by soda ash additions and by deairing. Although the wetting agent decreased the shrinkage somewhat, it was less effective than deairing or the addition of 0.2% of soda ash.

The percentage of increase in dry strength by these treatments should also reduce the cracking of the brick during firing, especially in scove kilns where there are excessive loads on the lower brick.

Table I shows that the absorption was decreased and that the treatment sometimes resulted in a change from a low-grade to a high-grade brick.

In the tests on fired strength, pugging with steam and hot water with an addition of 0.2% of soda ash produced the best results. Pugging with steam and hot water alone produced a maximum increase of 48% in strength; the addition of 0.2% of soda ash produced a maximum rise in strength of 39%. The combination of pugging with steam and hot water and an addition of 0.2% of soda ash was expected to give an 87% increase in strength; the actual increase, however, was 144%. The steam and hot water probably increased the reaction of the soda ash in the body, and the combined treatment, therefore, was more efficient than when either was used alone.

Most secondary clays consist of agglomerates of fine clay particles which are often firmly cemented together and therefore resist disintegration when they are mixed with water; the agglomerates in flint clays, for example, are thus cemented. Slate, shales, and semi-flint clays are also composed of agglomerates of clay particles and impurities firmly cemented. Plastic clays, such as stoneware clays, often resist disintegration to a marked degree when they are pugged with water, especially when they are calcareous in nature. China clays and kaolins, which are, usually composed of agglomerates of clay particles knit loosely together, disintegrate readily when they are placed in water.

Unless these agglomerates of clay particles are dispersed in the preparation of the body, the potential strength of the bond clay is never fully developed, and in some cases the ware does not have sufficient strength. One method of disintegrating these agglomerates is by mechanical means, such as wet grinding for long periods of time. A Maryland flint, for example, could be made almost as plastic as a ball clay by wet grinding for 2 hours with 1% of NaOH and 1% of dextrine and by screening through a 150-mesh sieve.[2]

[2] H. G. Schurecht, "Use of Electrolytes in Purification and Preparation of Clays," *Bur. Mines Tech. Paper*, No. 281, 47 pp. (1922); p. 39; *Ceram. Abs.*, 1 [9] 234 (1922).

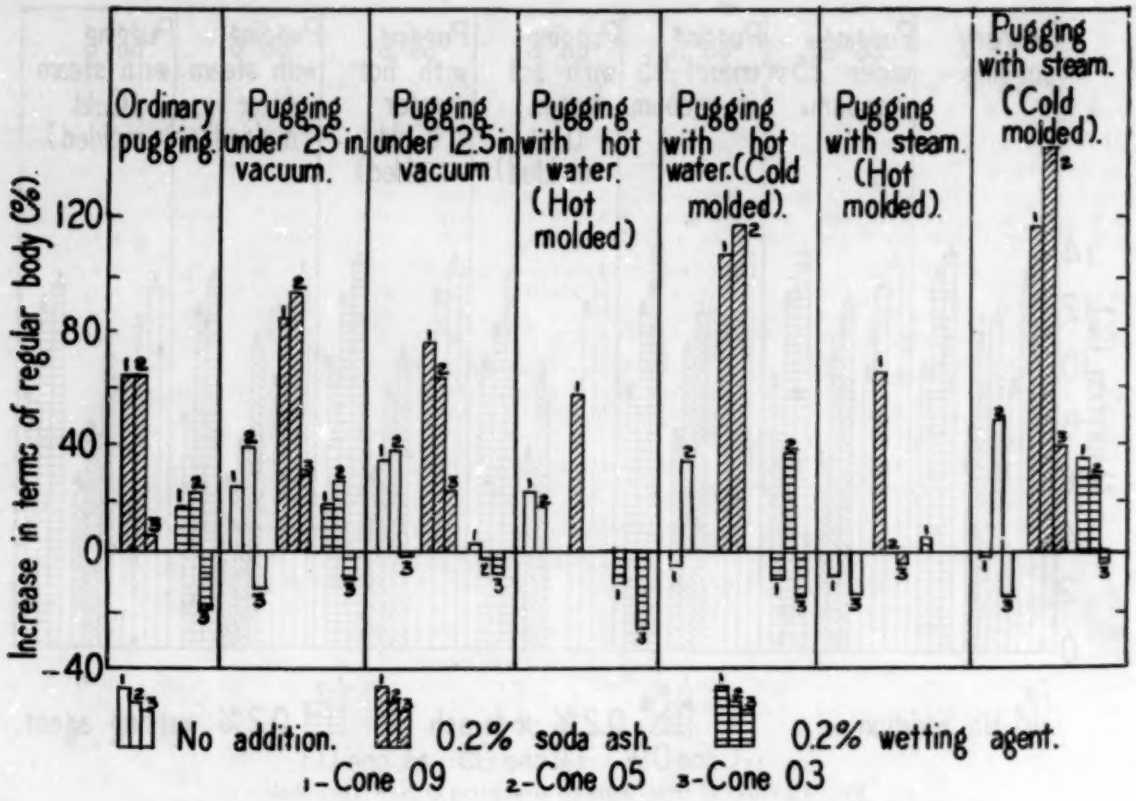

FIG. 4.—Effect of treatments on fired transverse strength of New York shale.

Another method of accelerating the disintegration of clay agglomerates is by the use of hot water in pugging as shown in the present work. The surface tension of water at 0°C. is 75.64 dynes per cm. and 60.75 dynes per cm. at 90°C. The viscosity of water at 0°C. is 17.93 millipoises and 2.83 millipoises at 90°C. This decrease in surface tension and in the viscosity of water permits it to penetrate and wet the clay agglomerates to a greater extent and thus facilitates the clay disintegration. The clays are therefore finer grained, which permits closer packing of the particles and greater strength.

The properties of clays are changed considerably by base exchange and by controlling their pH values. The addition of soda ash, therefore, causes a considerable increase in strength of the clayware. Pugging with hot water results in a finer-grained clay which raises its base-exchange capacity. The strengthening of the clay caused by the soda ash treatment was increased by pugging with steam and hot water. By using steam and hot water with soda ash, a greater increase in strength was obtained than was expected from a consideration of the sum of the increases produced when steam and hot water and soda ash treatments were used alone.

The improvements made by the use of wetting agents were also probably the result of the greater penetrating power of the water which contained the wetting agent because of the ability of the water to wet the clay particles more thoroughly. The wetting agent used in the present studies, however, was not so effective as soda ash in increasing the strength of the clay.

IV. Summary and Conclusions

A New York Chemung clay was used in the present studies. The results, therefore, apply strictly only to this clay, but because it is a typical brick clay, they may also be applicable to many other clays.

(1) Among the individual treatments, pugging with steam and hot water produced the greatest increase in fired strength, in one case to 48%. The addition of 0.2% of soda ash ranked next, producing a 39% increase; deairing raised the strength as high as 37.4%; pugging with hot water increased it 23.3%; and the addition of 0.2% of wetting agent raised the strength 21.4%. The treatments that produced the greatest fired strength, in general, required less water to work them; the clays also had lower drying shrinkage, a lower ratio of shrinkage to water of plasticity, and lower fired absorption. These clays, furthermore, showed the largest increase in dry density, dry strength, and fired density.

(2) The combined treatments produced the most efficient results. Pugging with steam and hot water with 0.2% of soda ash in one case increased the fired strength 144%. Pugging with hot water with 0.2% of soda ash raised the strength 116%. Deairing with 0.2% of soda ash produced an increase of 91.7%.

Pugging with steam and hot water and using 0.2% of wetting agent produced a maximum increase of 33%; and deairing with an added wetting agent raised the strength 25.7%.

(3) Most of the treatments apparently produce improvements in the properties of the bodies. In many cases, moreover, these treatments may be the means of improving the quality of the ware, reducing production costs, and lowering manufacturing losses. The treatments may also be used to improve the quality of low-grade building brick.

Acknowledgment

The authors wish to acknowledge their indebtedness to M. E. Holmes for helpful suggestions during the progress of the work.

CERAMIC EXPERIMENT STATION
NEW YORK STATE COLLEGE OF CERAMICS
ALFRED, NEW YORK

EXPANSION, CONTRACTION, AND STRENGTH CHANGES OF SOME CLAYS DURING FIRING*

BY R. K. HURSH AND M. K. BLANCHARD

ABSTRACT

The objective of these experiments was to determine (1) the linear changes in expansion and shrinkage during firing, (2) the effect of compressive loading on these changes, and (3) the variations in strength at furnace temperatures during the firing of some typical shales and fire clays used for the manufacture of structural clay products.

I. Introduction

(1) Materials

The materials used for the tests were two fire clays, designated as fire clay A and fire clay D, and two shales, E and S.

Fire clay A had a fine-grained texture, high plasticity, and excessive shrinkage, and it dried with considerable difficulty. This clay, which was principally kaolinite, also contained a considerable quantity of fine pyrite and a moderate amount of finely divided quartz.

Clay D, a hard siliceous fire clay, had moderate plasticity and low drying shrinkage; free quartz was present in large amounts and varied in particle size. Pyrite and siderite with calcite and small amounts of plagioclase feldspar were also present as well as a rather large amount of "sericite-like" material identified as "illite" under the classification of clay minerals by Grim.[1]

The red-firing shale, designated as shale E, had moderate plasticity and a marked tendency to laminate in stiff-mud molding because of its grain structure and platelike or micaceous character. Some free quartz and other impurities were also present.

Shale S had rather coarse grain, low plasticity, and a considerable amount of free quartz and iron-bearing minerals.

(2) Linear Expansion and Contraction

Measurements of linear changes of the clays during heating were made, with and without compression loading, in a vertical tubular furnace which had a Chromel wire resistor. The linear expansion and contraction were determined by a method similar to that of Chesters.[2] Figure 1 shows the cylindrical specimen, $^3/_4$ in. in diameter and $1^1/_2$ in. long, placed on a shelf of

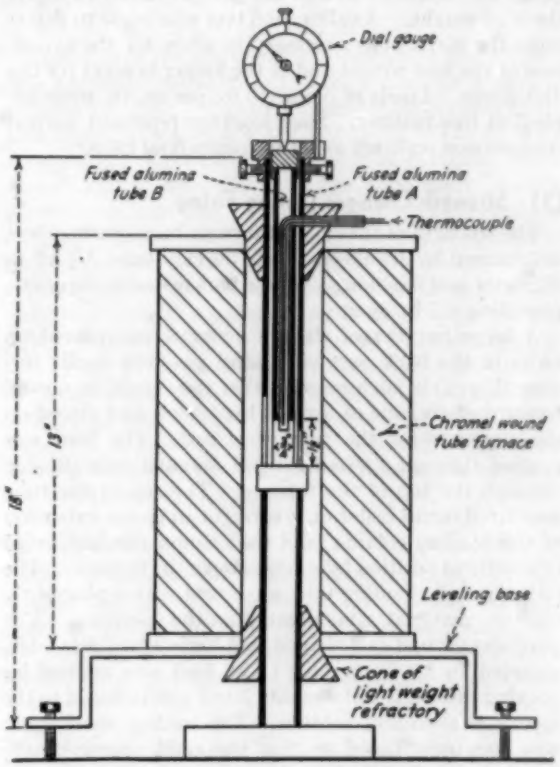

FIG. 1.—Equipment for determining thermal expansion and contraction.

* Presented at the Forty-First Annual Meeting, The American Ceramic Society, Chicago, Ill., April 18, 1939 (Materials and Equipment Division). Received April 18, 1939; revised copy received January 12, 1942.

[1] R. E. Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939).

[2] J. H. Chesters and C. W. Parmelee, "Measurement of Reaction Rates at High Temperatures," *ibid.*, **17** [3] 50–59 (1934).

fused alumina which rests in slots cut in the outer fused alumina tube, *A*. This tube rests on a solid base beneath the platform which supports the furnace. Placed on top of tube *A* and above the furnace is a dial gauge, supported by a brass collar and clamped to it by set-screws to insure rigidity. The plunger of the dial gauge rests on the brass cap on the inner fused alumina tube, *B*, which, in turn, rests on the specimen. A thermocouple passes through a slot in tube *B* and extends down through the bottom into a hole in the specimen. The top and bottom of the furnace are sealed against air currents by bushings of refractory insulation material.

Linear changes of the specimen are transmitted through tube *B* to the dial gauge. Because the inner and outer tubes are at nearly the same temperature, the thermal expansion of *B* is balanced by that of an equal length of *A*. The contraction or expansion indicated by the dial gauge, therefore, is the difference in linear change of the specimen and that of an equal length of tube *A*.

A preliminary calibration was made with a material of known thermal-expansion characteristics and with the same length as the test specimen. The specimen was heated (using rheostat control) at a uniform rate of 7.4°F. per minute, and temperature and dial-gauge readings were taken at 10-minute intervals up to the maximum of 2000° to 2200°F.

To determine the effect of compressive load on the linear changes of the specimen, a lead weight was placed on top of tube *B*, and the supporting arm for the dial gauge was extended so that the plunger rested on top of the lead weight. A calibration test was made to determine the corrections necessary to allow for the expansion of the lead weight and of the longer bracket for the dial gauge. Loads of 5 and 10 lb. per sq. in. were applied in this manner. Such loadings represent normal compression on brick as set in commercial kilns.

(3) Strength Changes During Firing

The strength of the clays at furnace temperatures was determined by transverse tests on clay bars, $^1/_2$ in. in diameter and 6 in. long. These bars rested on supports, providing a 5-in. span.

A large number of these specimens was placed on racks in the back part of a small gas-fired muffle furnace (Fig. 2) in such position that they could be moved forward easily, one at a time, by a hook and placed on the supports for the transverse test. The load was applied through a vertical fused alumina tube passing through the top of the furnace. The top of the tube was fitted into a collar on a wrought-iron pipe extension of this loading column, and the column was supported in a vertical position by guides above the furnace. The bottom of the loading tube was fitted with a plug of refractory material, which rested on the specimen. The plug was ground and shaped to a horizontal knife-edge, rounded to $^1/_{16}$-in. radius. The load was applied by pouring sand at a uniform rate into a pan fastened to the top of the loading column. The loading mechanism was counterbalanced so that the sand charge constituted the applied load on the specimen.

The furnace was heated at a uniform rate of 230°F. per hour, and five bars were broken at temperatures of 600°, 800°, 1000°, 1200°, and 1400°F. The transverse strength was calculated by the formula for a centrally loaded beam of circular cross section as follows:

FIG. 2.—Equipment for measuring hot transverse strength.

$$S = \frac{Mc}{I} = \frac{8Wl}{d^3}.$$

W = load (lb.).
l = span length (in.).
d = diam. (in.).
S = transverse strength (lb./sq. in.).

(4) Preparation of the Clays

The clays were ground to pass 20-mesh, tempered with 25% of water, wedged, and aged for 24 hours in a damp closet. Specimens for linear deformation tests were extruded through a $^3/_4$-in. die, dried to the leather-hard state, and cut to $1^1/_2$-in. lengths. After drying at 220°F., they were measured to 0.001 in. with a micrometer caliper. Specimens for hot transverse tests were extruded from a $^1/_2$-in. die, dried in troughs to insure straightness, and cut to length when they were leather-hard. The diameter of each specimen was measured by a Vernier caliper before it was placed in the furnace.

II. Results

The linear expansion and contraction measurements taken during the heating of each of the clays with and without compressive loading, as well as the results of the transverse-strength measurements at several temperatures, are shown in Fig. 3.

(1) Clay A

The expansion of clay A was somewhat less than that of the other samples, and a noticeable dip in the curve occurred between 1300° and 1600°F., which was not

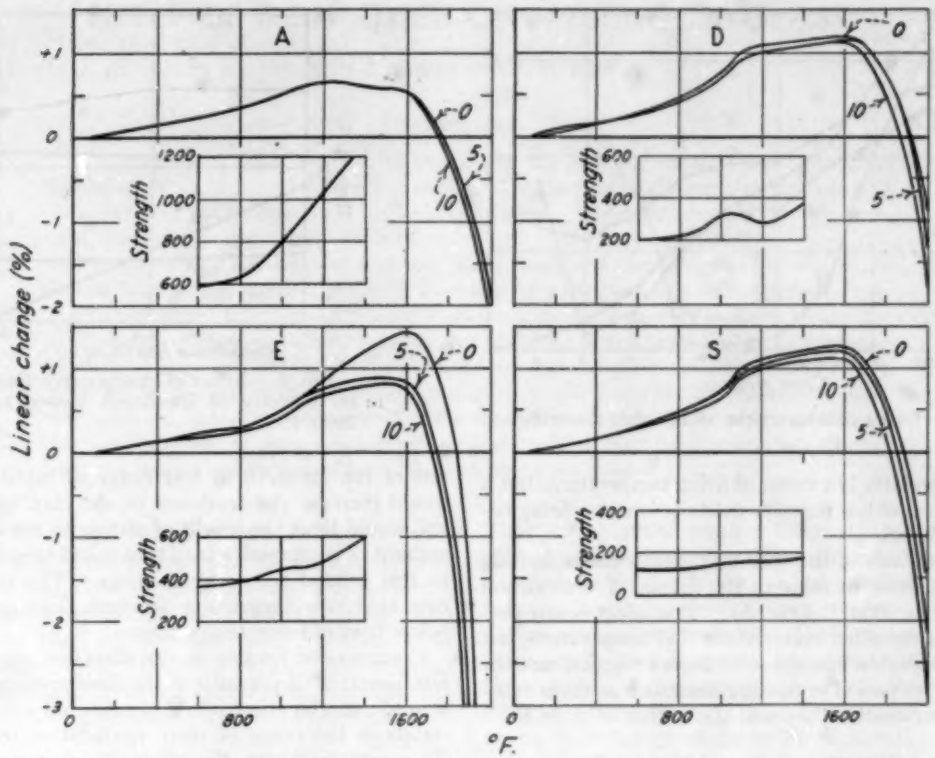

FIG. 3.—Linear expansion and contraction and transverse strength of clays at different temperatures.

found with the other materials. This dip apparently was the result of a shrinkage of the colloidal matter in the clay, which began at a lower temperature and was sufficient to offset the expansion due to the inversion of the fine-grained quartz around 1050°F. The setting of the colloidal matter resulted in the initial shrinkage of the body at 1300°F. before any fusion became apparent.

The high content of colloidal matter in the body accounted for its high initial strength, and the setting effect of heat caused the extremely rapid increase in strength above 800°F. The effect of compressive loading was not noticeable below 1600°F., and shrinkage above this temperature was only slightly increased with a load of 10 lb. per sq. in.

(2) Clay D

The other fire clay, clay D, showed a marked increase in rate of expansion in the quartz inversion range and a definite decrease in strength at 1200°F. Compressive loading decreased the expansion of this material above 600°F. Inasmuch as it had a much lower content of colloidal material and a high sand content, the decrease in expansion was apparently due to a packing of the weaker bonded granular material under compression.

(3) Shale E

The pronounced expansion of shale E, heated without load from 1200° to 1600°F., might be due to physical changes in the platelike particles which characterize this material, similar to that in the secondary expansion of some fire clays. When compressive load was applied, this abnormal expansion did not occur. The packing arrangement of these flat grains was evidently readjusted under pressure, and the individual particle growth was inhibited. Some glass of high thermal expansion might possibly be formed in this temperature range inasmuch as this shale had an unusually low maturing temperature. The presence of some melt, moreover, would readily account for the effect of pressure in reducing the expansion. The gain in hot strength in this range of temperature, however, indicates that no appreciable amount of fusion occurred. Compression under load and increase in hot strength would seem, therefore, to result from particle packing adjustment. A lag in the strength curve was evident in the range of the quartz inversion.

(4) Shale S

Shale S had very low initial strength and gained only slightly up to 1400°F. The effect of the quartz inversion on expansion was especially noticeable. Compressive loading decreased the expansion throughout the heating range and increased the initial rate of shrinkage above 1600°F.

(5) Porosity Changes

The general firing characteristics of the four clay materials are shown by porosity curves in Fig. 4. Shale E

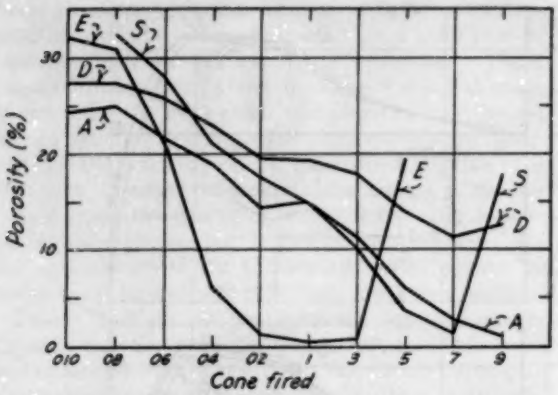

FIG. 4.—Firing characteristics of the clay materials.

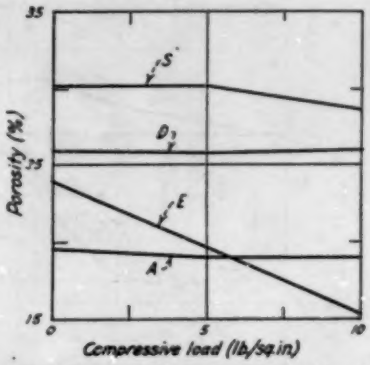

FIG. 5.—Effect of compressive load on porosity of specimens heated to 2000°F.

has a particularly low range of firing temperature, but a good interval of low porosity exists before overfiring become apparent.

Along one axis of the specimen, compressive loading causes a definite increase in the degree of vitrification of shale E at 2000°F. (Fig. 5). This effect is not pronounced in the other materials at this temperature, but it would probably become so at higher temperatures or with a longer period of heating inasmuch as these vitrification temperatures are well above that of shale E.

III. Discussion of Results

A definite compression or creep occurs in these clay bodies under such compressive loads as ordinarily exist in the setting of brick in kilns. This is evident from the decrease in expansion above 400°F. or higher. Although the maximum expansion is decreased, the temperature at which shrinkage becomes apparent is not usually lowered appreciably. The total permanent shrinkage in the direction of pressure is definitely increased above 1700° or 1800°F., but the rate of shrinkage remains about the same as that when no load is used, as shown by approximate parallelism of the curves.

A considerable decrease in hot strength of clay bodies might be expected in the range of dissociation of the clay minerals and of quartz inversion. This decrease is quite evident in the sandy fire clay D, and it is slightly apparent in both of the shales, but it is not found in the plastic and highly colloidal fire clay A. An appreciable loss of hot strength in this range of rapid expansion would increase the tendency of the clay to fire crack and would limit the height of setting in the kiln by the amount of compressive load that could be safely carried in this critical temperature range. The results indicate that the compressive strength does not decrease below that of lower temperatures.

Compressive loading in one direction caused a definite lowering of porosity of the fired specimen in shale E, and a similar effect would be expected with other materials in the range of their vitrification temperature. To a certain extent, the effect of pressure will be the same as that of increased temperature. The shrinkage and degree of vitrification of the lower ware in a downdraft kiln will be partially equalized with that in the hotter top portion as a result of the load applied by the ware that it supports. When unequal heating occurs in different parts of a kiln, the increased shrinkage caused by compression may cause tipping or tilting of the setting in the hotter areas.

IV. Conclusion

The data presented show interesting characteristics of some structural clayware materials with respect to expansion and contraction, hot strength, and the effect of compressive loads similar in magnitude to those in the ordinary kiln setting.

DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

EFFECT OF IRON OXIDE ON MELTING OF GLASS*

By R. L. Shute and A. E. Badger

Abstract

The addition of small amounts of iron oxide (0.1 to 0.2%) to soda-lime-silica glass batches exerts a profound influence in increasing the output of glassmelting tanks as well as in favoring the production of higher quality glass. The color produced by this addition, moreover, is not objectionable for many uses of the ware.

The accelerated melting rate probably is the result of a chemical effect of iron oxide in the batch and a physical property possessed by such glass to absorb radiation from the flames more efficiently. Attempts to measure these effects were made by noting the melting rate of glasses which contain varying additions of iron oxide and by determining the temperature gradient that exists in glass when it is melted in a miniature tank. The presence of iron oxide aids melting and fining in crucible melts at 1200°C., but no effect was observed at higher temperatures. The measurement of temperature gradients in a pot holding 45 lb. of glass and heated by flames passing over the glass surface showed that the temperature gradient increases with iron oxide content.

I. Introduction

Marked differences in the melting rates of various glasses have been observed in commercial glass practice. Colored glasses are usually more difficult to melt and fine properly than are colorless "flint" glasses. The relative importance, however, in the glassmelting process of radiation from the flames and of conduction and convection in the molten glass has not been proved.[1] That glasses exhibit marked differences in some of these properties is evident from the colder furnace bottoms which exist in tanks used to melt colored glasses (a fact that is easy to verify).

Experiments have shown that colored glass cools more rapidly than flint glass[2] during the working process. Colored glass is also a more efficient radiator[3] as is to be expected from theoretical considerations, and it is therefore a better absorber for radiation. The temperature near the surface of the metal in a tank melting colored glass consequently has a tendency to be higher than that of colorless glass.

Traces of iron oxide are always present in ordinary glasses, but the Fe_2O_3 may be kept as low as 0.02 to 0.05% by the proper selection of refractories and batch materials. Such low iron glass requires a large heat input to the furnace and is prone to contain seeds and striae. If the iron oxide content is increased to about 0.1%, the glass produced has a higher quality, and a greater output may be obtained without an increase in fuel consumption. This minor change in glass composition also produces a marked change in the temperature distribution in the melt. The temperature in the working end of a furnace producing low iron plate glass in one instance decreased about

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Part of a report of an investigation on heat penetration through various molten glasses which was submitted by R. L. Shute in partial fulfillment of the requirements for the degree of Master of Science, Department of Ceramic Engineering, University of Illinois, Urbana, Ill.

[1] Convection currents in a commercial melting tank were shown to exist by G. V. McCauley in "Fundamentals of Heat Flow in Molten Glass and in Walls for Use Against Glass," *Jour. Amer. Ceram. Soc.*, **8** [8] 493–504 (1925); and the importance of convection currents as a medium of heat transfer is stressed by F. W. Preston in "Behavior—and Misbehavior—of Glass in Tanks," *Bull. Amer. Ceram. Soc.*, **15** [12] 409–33 (1936). Experimental evidence, however, published later by R. Halle, E. Preston, and W. E. S. Turner on "Distribution of Temperature in Molten Masses of Colored and Colorless Glasses," *Jour. Soc. Glass Tech.*, **23** [97] 171–96T (1939); *Ceram. Abs.*, **19** [4] 89 (1940) has shown that the effect of convection currents has little significance in a laboratory-scale test similar to that published here. The account of Halle and his colleagues includes an extensive review of literature as well as experimental data.

Other important articles on this subject are as follows: (*a*) F. F. S. Bryson, "Distribution of Temperature and Block Corrosion in Glass Tank Furnaces," *Jour. Soc. Glass Tech.*, **13** [50] 140–66T (1929); *Ceram. Abs.*, **9** [5] 353 (1930).

(*b*) G. Gehlhoff, W. Schneekloth, and M. Thomas, "Currents and Temperatures in Glass Tanks, I," *Jour. Soc. Glass Tech.*, **15** [57] 12–29T (1931); *Ceram. Abs.*, **10** [8] 553 (1931).

(*c*) W. Trinks, "Economy and Capacity of Glass Tanks, Effect of Flame Luminosity and Other Variables," *Ind. Eng. Chem.*, **25** [8] 865–70 (1933); *Ceram. Abs.*, **12** [10–11] 366 (1933).

(*d*) F. G. Schwalbe, "Depth of Heat Penetration in Molten Glass with Luminous and Nonluminous Flames," *Ind. Heating*, **2** [2] 99–102; [3] 153–54; [4] 209–10 (1935); *Ceram. Abs.*, **14** [8] 155 (1935).

(*e*) C. Cone, "Heat Transfer in Glass Tanks," *Ceram. Ind.*, **27** [1] 34–42 (1936); *Ceram. Abs.*, **16** [9] 271 (1937).

[2] (*a*) W. E. S. Turner and F. Winks, "Study of the Casing of Colorless by Cobalt Blue Glass: II, Question of Setting Rate," *Jour. Soc. Glass Tech.*, **12** [45] 75–82T (1928); *Ceram. Abs.*, **8** [1] 24 (1929).

(*b*) S. English, H. W. Howes, W. E. S. Turner, and F. Winks, "Influence of Iron Oxide on Properties of Glass," *Jour. Soc. Glass Tech.*, **12** [45] 31–51T (1928); *Ceram. Abs.*, **8** [1] 23 (1929).

(*c*) I. I. Kitaigorodskii and N. W. Solomin "Rate of Setting of Glass During Working," *Jour. Soc. Glass Tech.*, **18** [72] 323–35T (1934); *Ceram. Abs.*, **14** [8] 187 (1935).

(*d*) O. G. Burch and C. L. Babcock, "Effect of Glass Color on Setting Rates in Manufacture of Glass Bottles," *Jour. Amer. Ceram. Soc.*, **21** [10] 345–51 (1938).

[3] W. Eitel and B. Lange, "Determining Radiating Power of Glass," *Glastech. Ber.*, **10** [2] 78–80 (1932); *Ceram. Abs.*, **11** [6] 358 (1932).

85°C. when a change was made to high iron plate and the melting temperature remained the same. Table I shows a factory record, previously unpublished, which may be adduced as additional evidence of the accelerated production resulting from the presence of small amounts of iron oxide in the glass.

TABLE I

FACTORY RECORD SHOWING ACCELERATED PRODUCTION OF GLASS WITH IRON OXIDE ADDITIONS

	Kind of glass melted		
	Low iron plate	High iron plate	Window
Melting area (sq. ft.)	1040	990	1304
Amount melted in 24 hr. (tons)	64	87	73
Melting area/ton (sq. ft.)	16.3	11.4	17.9
Heat required to melt 1 ton (B.t.u.)	23,490,000	16,270,000	18,430,000
Iron oxide (%)	0.035	0.25	0.1

The increase in the melting rate produced by small amounts of iron oxide in glass may be due to the greater absorption of radiation from the flames by such glass and also to a chemical fluxing action of iron oxide in the glass batch. The results of the measurement of these two factors are given in the following sections.

II. Measurement of Heat Penetration

The vertical temperature gradient in glass in a large tank furnace, which depends on radiation from flames and from the superstructure of the tank, cannot be duplicated in a small-scale test. A pot of moderate size, however, may be used in laboratory tests to provide comparative results of the heat penetration through various kinds of molten glass.

A cylindrical melting pot was used, which was about 15 in. deep, with an inside diameter of 10 in.; its capacity was about 45 lb. of molten soda-lime-silica glass to a depth of approximately $7^1/_2$ in. The pot was insulated with a 4-in. covering of firebrick. The space above the glass in the pot was used as a combustion chamber for gas which was introduced through a hole in the side of the cylinder. A burner was mounted outside this hole in such a position that the gases entered the combustion chamber, swirled around inside the cylinder, and escaped through a hole in a refractory cover which had been placed over the pot.

The temperature gradient in the molten glass was obtained by means of a Pt-Pt Rh thermocouple with bare tip, which was mounted on a movable frame with a scale attached so that it could be introduced through the hole in the cover of the pot. The depth of immersion of the tip of the thermocouple could be controlled, and the temperature gradient in the molten glass along the axis of the pot could be determined. The general procedure was to allow the temperature of the glass to reach equilibrium and to measure the temperature gradient by lowering the thermocouple into the glass and noting the temperatures at intervals of 1 cm. The temperature measurements were repeated on the upward traverse of the thermocouple through the glass.

III. Measurement of Heat Penetration in Glass in Relation to Iron Oxide Content

The melting pot was filled to the desired depth with low iron, plate-glass cullet, which had an approximate composition of SiO_2 72, CaO 10, MgO 4, Na_2O 14, Al_2O_3 1, and Fe_2O_3 0.035%. The percentage of Fe_2O_3 was obtained from chemical analysis and that of the other ingredients from batch calculation. The temperature gradient was measured along the axis of the pot after temperature equilibrium had been attained. Because temperature measurements were found to fluctuate above and near the surface of the glass, the initial measurement at approximately 1400°C. was made 1 cm. below the surface.

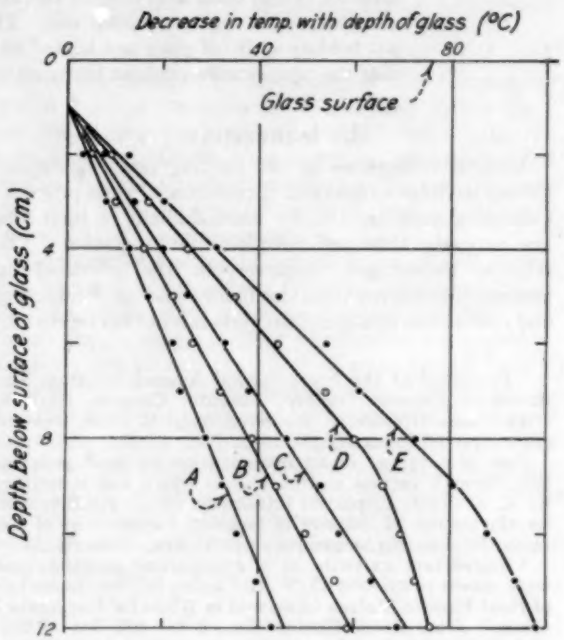

FIG. 1.—Temperature gradients in molten soda-lime-silica glasses which contain varying amounts of iron oxide; decrease in temperature with depth of glass is based on starting position 1 cm. below glass surface, at which point the temperature is approximately 1400°C. in all cases; amount of iron oxide: curve *A*, 0.035%; *B*, 0.135%; *C*, 0.335%; *D*, 0.535%; and *E*, 1.035%.

Figure 1, curve *A*, shows the temperature gradient of this glass, and curves *B*, *C*, *D*, and *E* show temperature gradients under corresponding conditions after additions of 0.1, 0.3, 0.5, and 1.0% of iron oxide had been incorporated in the glass. These additions were made in the form of a high iron frit to facilitate their mixture with the molten glass. The series of curves in Fig. 1 shows that iron oxide has a pronounced influence in glassmelting processes by increasing the temperature gradient that exists in the melt. An amount of Fe_2O_3 as small as 0.1% is effective (compare curves *A* and *B*). The temperature gradients shown in Fig. 1 are composite results of the phenomena of conduction, convection, and radiation which exist in this experi-

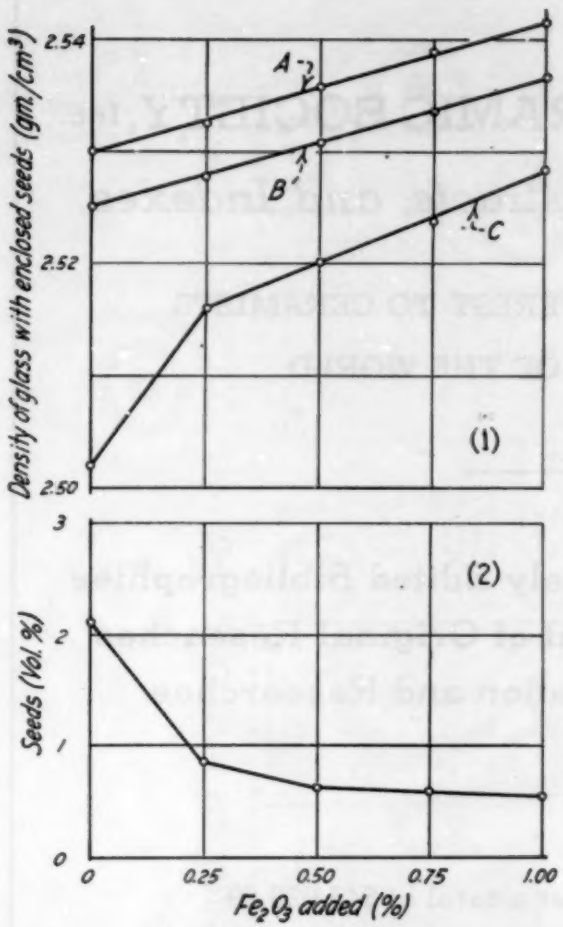

FIG. 2.—(*1*) Density of glass with inclosed seeds used to indicate extent of melting and fining; melting temperature: curve *A*, 1350°C.; *B*, 1275°C.; and *C*, 1200°C. (*2*) Percentage volume occupied by seeds in glasses, corresponding to density of curve *C*, shown in Fig. 2 (*1*).

mental setup. The relative importance of these properties, however, is not measurable by this method.

IV. Chemical Effect of Iron Oxide in Glass

The melting and fining rates of glasses were compared in order to investigate the possible action of iron oxide as a chemical flux in glass. A soda-lime-silica glass with a composition of SiO_2 72, CaO 12, and Na_2O 16% was used as a parent glass, and the batch consisted of potter's flint mixed with the carbonates of soda and calcium. Suitable additions of Fe_2O_3 were made to this parent batch to produce a series of five glasses containing 0.0, 0.25, 0.50, 0.75, and 1.0% of Fe_2O_3. Three series of 1/4-lb. melts were made in porcelain crucibles in 2-hr. periods at 1200°, 1275°, and 1350°C. After annealing, the densities of the glasses with inclosed seeds were measured by the method of hydrostatic weighing, and these densities were taken as a measure of the extent of the melting and fining of the samples. The results of the density determinations are given in Fig. 2 (*1*), in which curve *A* refers to melts made at the highest temperature, namely, 1350°C. All of these melts were seed-free, and curve *A* therefore represents the change in density produced by the presence of iron oxide in the glass. Curve *B* shows the densities of melts made at 1275°C., and all of these melts contained small seeds, the percentage of the total volume occupied by the seeds being about the same in each melt as shown by the parallel courses of curves *A* and *B*. Curve *C* of Fig. 2 (*1*) shows the densities of the series of glasses melted at 1200°C.; at this temperature, the presence of iron oxide had a noticeable effect in reducing the percentage volume occupied by the seeds. This effect is shown more clearly in Fig. 2 (*2*), on which the percentage volume occupied by seeds is given, corresponding to the densities of curve *C*, Fig. 2 (*1*). These results show that, at the melting temperature of 1200° C., the presence of iron oxide accelerates the melting and fining process, whereas no changes were measurable at the higher temperatures of 1275° and 1350°C.

V. Summary of Results

The presence of iron oxide in glass results in a steeper temperature gradient in the melting furnace. This greater drop in temperature as compared with low iron glass produces cooler tank bottoms, and a more shallow melting tank is the result. Commercial experience has shown that the presence of a small amount of iron oxide, such as 0.1%, produces a greater melting capacity in a tank furnace. Large amounts may decrease the output of high-quality glass by excessive temperature gradients in the melt which occur in a tank which is too shallow.

Iron oxide appears to favor the melting process by its chemical fluxing action if melting is carried out at a comparatively low temperature such as 1200°C. At high temperatures (1275° and 1350°C.), no chemical effect was noted.

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